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ERRATA

Page.	Line.	Read	for
19	Structure II		

| 19-20 | | The word " *dihydroxy artostenone* " should be read as " dihydroxy artostanone " throughout the paper. | |

| 219 | Structure II | | |

258	33	3-Amino-4-hydroxyphenylarsonic acid	3 Amino-2-hydroxyphenylarsonic acid
285	10	*Add* after solution " should readily give under light touch some solution "	
261	End of 3rd paragraph	*Z. physikal. Chem.*, 1939, **4B**, 299	*Z. physikal. Chem.*, 1929, 48, 299.
Facing 264		Fig. 1, the arrow should be shifted left coinciding the first line in that group of lines.	

		Read	*for*
269	6	author	author.
,,	7	(. . . 1940, 14, . . .)	(. . . 1929, 14, . . .).
,,	10	acetone	atetone.
290	Table I, column 4	$NH_4H[O(MoO_3)_{4.4}]$	$NH_4H[O(MoO_3)_{4.9}]$.
293	,, IVA. ,, 1	$Na_2[(OMoO_3)_8]$	$Na_2[O(MoO_{38})]$.
,,	., IVB. ,, 1	$Na_2[O(MoO_3)_8]$	$Na_2[O(MoO_3)]_9$.

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ELECTROCHEMICAL INDUSTRIES: POSSIBILITIES IN INDIA *

By B. B. Dey, D.Sc., F.R.I.C., F.N.I. '

The application of the electric current to chemical industry, apart from its use as a source of power, has become at the present time of such immense significance 'to modern life that its importance in the development of the great basic industries of this country would be manifest from a consideration specially of India's existing and potential mineral and power resources. It is indeed a far cry from the simple experiments with the voltaic pile conducted by Sir Humphrey Davy in the early years of the 19th century on the decomposition of caustic soda, to the present day prodigious plants of the Alcoa in Tennesse Valley and other places of the U.S.A. using up nearly a third of a million horse power, or the copper plants of the Chile Copper Company in Chuquicamata, Chile, or the high frequency induction furnaces of the Ajax-Northrup type used in alloy melting, where the only practicable limits to the temperatures reached are those imposed by the capacity of the materials of construction to withstand the temperatures created. Electrochemical industries cover to-day almost every field of national endeavour. The following list[1] of some of the more important materials turned out by the electrolytic cell and the electric furnace shows the astonishing range of their usefulness both in times of peace and in war. The finished products together with raw materials used in their manufacture and their applications, classified according to their mode of production, are given in Tables I-IV.

Table I

Products of the electrolytic cell

(a) Electroseparation.

Product.	Raw material.	Applications.
Chlorine	Salt, water	Bleaching, gas warfare, hydrochloric acid, chemical syntheses, sanitation.
Hydrogen	Caustic soda and water.	Balooning, hydrogenated fats.
Oxygen	,, ,,	Oxywelding, oxycutting.
Caustic soda	Salt, water	Soap, paper, dyestuffs, drugs, explosives.

(b) Electrolytic oxidation.

Product.	Raw material.	Applications.
Potassium chlorate	Potassium chloride	Matches and dyeing.
Potassium persulphate	Potassium sulphate	Oxidising agent, bleaching.
Perborates	Borax	Bleaching agent for textiles.
Sodium bichromate	Chromium salts	Dyeing and tanning.
White lead	Lead	Paint pigment.

(c) Electrowinning and refining.

Product.	Raw material.	Applications.
Copper	Copper ore, crude copper	Electrical and brass industries.
Zinc	Zinc ore	Brass industry, galvanising.
Manganese	Manganese ore	Ferrous and non-ferrous alloys
Tin	Impure tin, Tin dross.	Tinplate industry.
Gold	Anode slime from copper	Coinage, jewellery, industrial alloys.
Silver	Do	Do
Platinum	Nickel slimes	Catalysts, jewellery, alloys.

(c) Electrowinning and refining.

Product.	Raw material.	Applications.
Cadmium	Zinc electrowinning slimes	Plating, alloys.
Chromium (electroplating)	Chromic and sulphuric acids.	Plating.
Nickel	Crude nickel	Alloys, plating industry, dairy equipment, utensils.
Lead	Crude lead	Alloys, fittings, acid chambers

TABLE II

Products from fused electrolytes

Product.	Raw material.	Applications.	Product.	Raw material.	Applications.
Aluminium	Bauxite	Electric power transmission cables, light weight alloys for aeroplanes, automobiles, aluminothermic reactions, ammonal, acid containers, cooking utensils.	Sodium	Caustic soda or salt.	Peroxides, cynaides, bleaching, mining, alloys tetraethyl lead, organic synthesis.
			Barium	Barium chloride	Alloys, electron emission.
			Beryllium	Beryl	Light alloys.
Magnesium	Magnesium chloride or Magnesium oxide.	Light weight alloys, tracer bullets, flashlight powders and flares.	Cerium metal	Rare earth chlorides	Pyrophoric alloys, tracer bullets and shells.
			Thorium	Potassium thorium fluoride	Electron emission, X-Ray targets.

TABLE III

Products of the electric furnace

Product.	Raw material.	Applications.	Product.	Raw material.	Applications.
Alumina (fused)	Bauxite	Abrasives and refractories.	Ferro-vanadium	Iron vanadate	Special and automobile steel.
Quartz (fused)	Quartz rock	Optical uses, heat resisting materials.	Calcium carbide	Lime and coke	Acetylene for welding, cutting, lighting, for chemical synthesis - leading to plastics, synthetic rubber.
Graphite	Anthracite coal	Electrodes, lubricants.			
Ferrochrome	Chrome ore	Special and high speed steels, armour plate, projectiles.	Calcium cyanamide	Calcium carbide and nitrogen of air	Fertiliser, ammonia, cyanides.
Ferro-manganese	Manganese ore and coke	Steels, permanganates.	Carbon bisulphide	Coke and sulphur	Solvent, insecticide, carbon tetrachloride, artificial silk (viscose).
Ferrosilicon	Iron, silica and coke	Steels, acid resistant iron.			
Ferro-tungsten	Tungsten ore	Special and high speed steels.	Nitric acid	Air	Explosives, fertilisers.

TABLE IV

Organic products

Product.	Raw material.	Applications.	Product.	Raw material.	Applications.
Anthraquinone	Anthracene	Dyestuffs.	Benzidine	Nitrobenzene	Dyestuffs.
			Sorbitol	Glucose solution	Resin, plasticisers, Vitamin C synthesis.
para Amino phenol	Nitrobenzene	Dyestuffs, drugs and developers.	Mannitol	Do	Esters, ethers, chemicals.

Electricity thus enters into the production of a large variety of basic materials—metals, alloys and chemicals, fertilisers, abrasives, graphite electrodes, primary and secondary batteries, etc., many of which serve again as raw materials for other industries. In some of these the use of electricity is indispensable as in the production of aluminium, sodium, magnesium, calcium carbide, fused alumina, graphite, etc., while in others, it leads to a purer product and is more economical as in the production of copper, tin, lead, nickel, gold and ferro alloys and special steels.

During the past decade the production of metals and alloys has taken a steep upward turn chiefly because of improvements in the methods of manufacture, lowering in the costs of production, discoveries of new uses and development of backward areas. Table V gives figures for the world production of some of the important metals during the year 1937.

TABLE V[2]

Copper	2,434,000 short tons.	Aluminium	490,600 short tons.
Lead	1,893,000	Ferro alloys[3]	2,180,000 metric tons
Zinc	1,845,000	Magnesium[4]	25,000
Tin	205,200	Sodium (1940)[5]	50,000

In recent years an additional impetus has been provided by the War, the Aluminium Company of America (Alcoa) alone having produced in 1939, 146,000 tons[6] and embarked on an expansion programme involving an expenditure of 30,000,000 dollars, increasing the production to 178,600 tons in 1942. Similarly the Dow Chemical Company in U.S.A. with the support of the Government, has launched on the production of magnesium aiming at the target figure of 362,500 tons by the end of 1943 at a cost of 339,000,000 dollars.[7] In Germany the production of aluminium for the year 1937 was 127,500 tons accounting for a fourth of the total world output of this metal that year.[8] These figures convey an idea of the enormous scales on which some of the major electrochemical industries are being operated at the present day.

An abundant supply of cheap electrical power which is the raw material *par excellence* for this industry must be considered to be the most important single factor in the development of electrochemical industries in any country. A study of the current requirements for various electrochemical industries is, therefore, of great interest from this point of view. The following table in which the cost of electricity in relation to selling price of electrochemical and electrometallurgical products is given reveals the enormous quantities and the wide variations of the power utilized.

TABLE VI[8]

Product.	Kw. per ton.	Cost of current per ton. £	Approximate price per ton. £	Current cost as % of selling price.	Product.	Kw. per ton.	Cost of current per ton. £	Approximate price per ton. £	Current cost as % of selling price.
Ferromanganese	3500	2·3	19	12	Cadmium	2,250	1·5	270	0·6
Ferrosilicon	4500	3·0	11	27	Nickel	2,500	1·7	180	0·9
Ferrotungsten	8600	5·75	524	1·1	Lead (Refining)	100	0·07	15	0·5
Ferrochrome	7000	4·70	23	20	Calcium carbide	3,000	2·0	11	18
Aluminium	18,000	12·0	94	13	Chlorine	3,000	2·0	19	11
Magnesium,					Caustic soda	3,000	2·0	18	11
Electrolytic	20,000	13·4	168	8·0	Silicon carbide	8,500	5·7	39	15
Electrothermal	24,000	16·0	168	9·5	Aluminium abrasives	2,500	1·6	—	—
Sodium	15,000	10·0	—	—	Hydrogen	67,000	45·0	—	—
Beryllium	65,000	43·4	—	—	Sodium chlorate	6,700	4·5	30	15
Cerium	25,000	16·7	—	—	Potassium chlorate	5,800	3·9	36	11
Copper (extraction)	2,500	1·6	42	4·0	Graphite	3,900	2·6	—	—
Zinc	3,500	2·4	14	17					

It is obvious, therefore, that for the successful operation of any electrochemical industry, the cost of power should be as low as possible, and the controversy,[9] sometimes rather acrimonious, which is being carried on at the present moment regarding the relative merits

and economics of power generation by hydroelectric and thermal plants should be of special interest with reference to this country. According to one view [10] hydroelectric power can never be surpassed or replaced as the cheapest source of power for the following reasons :—

(1) In a hydroelectric station, the capital cost is made up by 20 per cent plant and the rest for dams, aqueducts, etc. The latter have an almost indefinite life. Hence in spite of increased capital cost the amortization rate is low. The reverse is the case with thermal stations in which over 75 per cent is plant and the rest buildings.

(2) The maintenance and running costs are low. In a thermal plant in addition to increased cost under the above heads must be added the heavy cost of fuel.

(3) At a hydroelectric station the maximum cost is known from the beginning while with steam, the price may vary with the price of coal or other fuel.

(4) The cost of electricity generated at a hydroelectric station with a capital cost of £. 49 per installed kilowatt is likely to be the same as at a thermal station with a capital cost of £. 18 per installed kilowatt because of lower amortization rates in the former case and increased maintenance and running expenses of the latter. (These figures apply more to Britain where the most favourable sites have been exploited already. Donkin gives the capital cost of hydroelectric stations as £. 35 per installed kilowatt in Great Britain, £ 36 in Canada, and an average roughly from £ 18 to £ 50 per installed kilowatt in U.S.A.

According to a comparative study made in 1936-38 in Scotland on the cost of power generated from water and of that from a steam plant situated in the neighbourhood of a coal field, with coal at 15 shillings per ton the cost of current by steam was double.[10] Another careful estimate of the comparative costs in the two cases has led to the conclusion that, excluding charges on capital, the cost in the case of water power plant was 0.015 d. per unit while that in the thermal plant was 0.96 d. per unit.

On the other hand, there is the other view[8] which is equally insistent about the thermal station having many decided advantages over the hydroelectric power station, the following being the main arguments advanced in favour of the thermal stations :

(1) Because of lower capital cost, the undertaking would be much less vulnerable to fluctuation on the demand for power.

(2) It would not be subject to compulsory stoppages due to drought or ice conditions.

(3) In many cases waste-heat is also required as in the production of aluminium from alumina and the thermal cost of energy may be reduced by half by proper co-ordination. The fuel consumption of modern boilers is extremely low, the best present day practice corresponding to 0.96 lb. of coal per kw. hr. The power output at existing thermal stations can be augmented to any desired extent by the installation of superposed high pressure boilers.

(4) In general the cost of transmitting electricity by power lines (Morrow, loc. cit.) is about 2½ times the cost of transporting fuels to distances of 50-100 miles. The advantage would, therefore, lie with the thermal generator situated at the load.

(5) The most favourable sites for water power development have already been tapped and future installations will be costlier.

We may now consider how far these arguments for or against hydroelectric or thermal plant affect our case. India's coal resources are known to be concentrated only in

certain in small areas, and the deposits which are not unlimited, are being used up at an alarming rate. With the exception of Germany where the immense deposits of lignite have perhaps been mainly responsible for retarding water-power development, electro-chemical industries have made the greatest headway in countries with extensive water power resources such as the U.S.A., Canada, the Scandinavian countries, Italy, France and Switzerland. It can hardly be disputed, therefore, that unless fresh deposits of coal are discovered in India at several sites situated favourably with respect to raw materials, our industries must depend to a large extent on hydroelectric power.[12] In Table VII the potential water power resources of different countries and the extent to which develop-ment has progressed are given.[10]

TABLE VII

Country.	H. P. potential.	Developed H. P.	Country.	H. P. potential.	Developed H. P.
Great Britain and Ireland	1,257,000	488,000	Germany	8,800,000	3,500,000 (1930)
			Switzerland	4,000,000	3,500,000 (1933)
Canada	34,000,000	8,845,000 (1942)	France	10,000,000	4,220,000 (1935)
Newfoundland	400,000	—	Italy	9,000,000	7,000,000 (1933)
South Africa	1,600,000	—	Russia	270,000,000	30,000,000 (1937)
India	27,000,000	500,000 (approx.)		(only 50% can be developed.)	
Norway	12,000,000	2,737,000 (1932)	U. S. A.	80,000,000	21,000,000 (1940)
		(since then great progress has been made.		(in 1943, an additional 5,000,000 H. P. would have been available from the new Federal Projects)	
Sweden	10,000,000	2,000,000 (1933)			

A glance at the table reveals the very backward position which India occupies in the matter of power development. It would be seen that as far as India is concerned, hardly 2% of her potential resources has been developed yet and there is nothing to prevent large schemes of expansion of water power being contemplated, undeterred by the argu-ments advanced against it in other countries. In areas deficient in such resources but with an abundance of cheap coal, as in Bihar or Bengal, thermal installations will necessarily get the preference.

In order to make the best use[10] of the water power resources of any country, it is necessary to have a comprehensive inland water survey involving (1) a systematic gauging of all important rivers, (2) rainfall and snow records and (3) a study of absorption, evaporation and ground storage. Such essential work must obviously be undertaken under state auspices in order that the information may have continuity and be available to all. In U. S. A. all such basic information is collected by the Weather Bureau and the Geological Survey which are departments of the Government. Till 1932, the develop-ment was left only to private initiative and enterprise, but since then the Federal Power Commission has launched vast schemes like the Boulder Dam and Grand Coulee Dam projects, which are designed not only for power supply but also for water supply and river regulation. Similarly, Canada, Switzerland, Italy and the Scandinavian countries have Government departments responsible for inland water supply. It is clear that a co-ordinating agency for obtaining and distributing correct basic information on all such matters must be established in this country before any systematic development of power on a large scale can be contemplated. From this point of view the development of electricity cannot possibly be relegated as a provincial subject. Unless the controlling interest

vests in the Central Government which alone can sponsor large schemes of power develop-
ment, there can be no prospect of a flourishing national electrochemical industry operat
ing in India on a competitive basis with those of other countries.

It is needless to state that India has still to find a place on the map of electrochemical
industries of the world. Plants for the production of caustic soda and chlorine are now
being operated by the I.C.I. at Rishra, the Tatas at Mithapur and by the Mettur Chemicals.[12]
In addition there may be several smaller installations for the manufacture of caustic soda
and chlorine as at the paper mills at Dalmianagar of the Rohtas Industries, with a
limited production for specific demands. Aluminium metal from Indian bauxite is also
being manufactured in recent years through the joint enterprise of the British Aluminium
Company, the Aluminium Company of Canada and others, but the exact figures of
production and current consumption are not available. Apart from these India does not
appear to have any other large electrochemical industries.

The import figures taken from the Annual Statement of the Sea Borne Trade of
British India for the year 1937-1939 issued by the D. G. Commercial Intelligence and
Statistics for some of the important materials which are mainly or exclusively produced
by electrochemical methods are given in Table VIII.

TABLE VIII

Product.	Weight.	Value.	Product.	Weight.	Value.
Aluminium unwrought, sheets and other manu- factures	66,832 cwts.	Rs. 52,70,222	Zinc Caustic soda Bleaching powder	446,657 cwt. Rs. 518,485 ,, 237,303 ,,	76,78,474 42,80,555 13,12,915
Ferro alloys	3,092 tons.	7,49,006	Chlorine (liquid)	668,428 lbs.	2,49,220
Copper, unwrought, wrought and wire exclu- ding telegraph wire	316,063 cwts.	1,39,79,489	Calcium carbide Potassium chlorate Sodium bichromate	54,445 cwts. 42,207 ,, 20,762 ,,	5,94,122 7,07,912 4,65,925
Lead	156,018 ,,	28,87,032			
Tin	60,415 ,,	85,47,596		Total Rs.	4,67,22,468

It will be interesting to examine how far our position in regard to the raw materials
required for these electrochemical industries warrants the import in large quantities of the
products of these industries into India.

Aluminium.—Bauxite has so far been the only source for the production of this metal.
To quote the Records of the Geological Survey of India (Volume 70, page 352, 1936) "The
Indian bauxite industry has never been actively developed in spite of several efforts, justi-
fied by the large occurrences of this material in various parts of the peninsula. The trade
so far has depended on small orders from oil companies for the purification of kerosene,
and smaller demands by chemical companies for the preparation of aluminous sulphates,
etc." Discussing the industrial possibilities of Indian Bauxite, Chatterjee, Roy and
Das-Gupta[13] state that the available deposits are low in silica, high in titanium oxide,
of moderate iron content and lend themselves readily to treatment by the Bayer process
and 95 per cent of the alumina are recoverable. As far as our present knowledge goes,
India is deficient in copper, tin and zinc but bauxite of good quality is available in
enormous quantities at several places and the use of aluminium and aluminium based
alloys in place of copper and its alloys should be extremely desirable in the interests of
this country.

. · *Magnesium.*—The raw materials for magnesium production are usually magnesite or dolomite which are converted into the chloride before electrolysis, or magnesium chloride itself where it is available. Extensive deposits of magnesite of very high purity are known to occur in the Salem District (Madras). This material should lend itself very well to treatment by the "Oxide process" which after receding into the background for some years appears to have gained in importance during the last few years. The Austro-American Magnesite Company at Radentheim have been operating this process[14], with a power consumption of 23 kw. hr. per kg. of metal ingot (including 4 kw. hrs. for keeping hydrogen in the flue) as against the 25 kw. hr. required for the chloride process. For the processing of the cheap magnesium chloride of the Tatas at Mithapur a modified Dow process may prove suitable.

Manganese.—Manganese ore of high quality is available in large amounts in India. The export of manganese ore in the year 1937-1938 amounted to 1,001,096 tons with a value of Rs. 2,21,28,945. In this connexion, the development recently of an electrolytic method for the extraction of manganese [15] should be of particular interest in this country.

Chromium.—Chromite ore of good quality is available chiefly in Baluchistan, Mysore and in Bihar. The export of chromite ore in 1937-1938 was 41,452 tons with a value of Rs. 12,69,078. The production of ferrochrome and sodium bichromate is a distinct possibility.

Caustic Soda, Chlorine and Bleaching Powder.—Extensive deposits of salt are available in several parts of the country and some of them are favourably placed with regard to power. Expansion in the production of caustic soda can be achieved without difficulty but the disposal of chlorine may remain a problem for some time till increased activity in other fields of chemical industry and in sanitation leads to greater use.

Calcium Carbide.—The raw materials for the production of calcium carbide are limestone and coke. Limestone of high quality is available in almost every province and the substitution of charcoal, if available at cheap prices, for coke has been found to lead to smoother furnace operation and to a purer product. The production of calcium carbide in this country will depend mainly on the location of the factory in places favourably disposed in regard to power.

Organic Compounds.—Although in bulk and value, organic products cannot compare with the inorganic products cited above, they find such important uses as dye intermediates, photographic developers and drugs that it is very regrettable that so little prominence has been given to the manufacture of organic compounds by electrolytic methods. This is not because electrolytic methods have not been employed in organic industries—in fact numerous applications have occurred—but to quote Thatcher[16], one of the pioneers of technical electrochemistry in America, "It will probably be difficult if not impossible to cite another branch of applied science in which such extreme reticence has been maintained". The typical reactions of organic chemistry like reduction, oxidation and substitution may often be carried out with ease if not elegance by electrolytic methods. Expensive reducing or oxidising agents like zinc, tin, lead peroxide, or chromic oxide are dispensed with and there are no sludges of inorganic bye-products to remove. Once the right conditions for a particular desired result have been determined the electrolytic method has proved superior to the chemical method because of the greater ease of control over the reaction.

It would appear from the report of the raw material position for the dyestuffs industry in India by Pai and Venkataraman[17], in which a promising survey has been made of the availability of the primary materials like benzene, toluene, naphthalene, etc., that the application of electrochemical methods to the production of technically important organic compounds is another promising field lying unexplored. Researches on the manufacture of dye-intermediates like benzidine, tolidine and dianisidine and of *para-*aminophenol which have been in progress for the past three years in the Chemistry laboratories of the Presidency College, Madras, under the auspices of the Board of Scientific and Industrial Research have proved beyond doubt that both benzidine and aminophenol, the production of which have been carried out on a pilot plant scale, can be manufactured satisfactorily by the electrochemical method which is superior in ease of operation, purity of product and cost of production to the chemical method.

The raw material resources in respect of several electrochemical industries are satisfactory. The deficiencies of copper, zinc and tin are serious, but by increased use of aluminium, as is being done at present in other countries deficient in copper, this can be overcome. While the Geological Survey of India has done very valuable work, its activities, as has been pointed out by many eminent scientists and industrialists, have been on a scale wholly inadequate for achieving great results for a subcontinent like India.

As regards power, while it is insufficient at the present time for operating electrochemical industries on a large scale, the proposed priority for the development of power in post-war reconstruction should make sufficient power available in the near future, for the creation of a number of first rate electrochemical industries. Similarly the deficiency of the very limited technical knowledge and skill in the country for operating electrochemical plants should be largely remedied by the proposal of the Government to establish a central Electrochemical Research Institute, and to depute a large number of science graduates abroad for training in industrial research. The extent to which the major electrochemical industries have developed in advanced countries has been the result of the closest collaboration between the Engineer, the Metallurgist and the Chemist and any planning for the establishment of electrochemical industries will necessarily have to be done in close co-ordination with planning for other industries in India. Thus, while the development of power is essential for electrochemical industries, it will also benefit agriculture by development of irrigation, not to mention numerous other industries using power and also the house-hold consumer. Similarly, if a reliable survey is made of the mineral wealth of this country, the major beneficiaries will be other industries, chemical and otherwise, besides the electrochemical industries.

From the considerations set forth in the preceding paragraphs, it appears that the following steps are urgently called for as essential preliminaries to the establishment of electrochemical industries in this country :

(1) A re-examination of the water power resources of India by a Central Water Power Commission with experts from America and Europe in the staff and aided by departments like the Geological Survey of India and the Metereolological department. The report that Mr. W. L. Voorguin, Chief of the Project Planning Division, T. V. A. would shortly arrive in India to advise the newly constituted Central Technical Power Board is most welcome from this point of view.

(2) A survey of the mineral wealth of this country on a much more extensive and intensified scale should be undertaken. The example of the U. S. S. R. provides an excellent model to work upon.

(3) Wherever the position relating to availability of raw material and power is favourable, as in the case of the manufacture of aluminium, magnesium, caustic soda, calcium carbide, etc., the manufacture of these materials should be undertaken under state auspices.

(4) The establishment of one or more electrochemical research institutes headed by experts to solve problems of the electrochemical industry as they arise and to do exploratory work for the exploitation of local raw materials.

(5) The immediate training of a large number of Indians in electrochemical industries in America and Europe by agreement with the industries concerned, on suitable terms.

(6) A comprehensive survey on the availability of raw material for electrochemical and electrometallurgical industries in places where there are projects for power development.

Whether India by her own efforts unaided by other advanced countries, can attain a place of eminence in this industry worthy of her raw material resources, her potential reserves of power and her great population seems at present to be doubtful. It should not, however, be difficult to devise a scheme of co-operation of the Indian industry with other well-established foreign firms, both in the matter of capital and technical skill and knowledge on suitable and equitable terms. It is hoped that those in charge of planning will launch on carefully drawn and co-ordinated projects, with boldness and imagination for the results to be achieved are no less than the happiness and prosperity of the people of this country.

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PHYSICO-CHEMICAL STUDIES ON HAEMOLYSIN. PART V. ON THE COMPOSITION OF HAEMOLYSIN

By S. S. De

The molecular weight of haemolysin has been determined to be 35,200 from diffusion experiments. The estimation of the different amino acids was carried out and it was found that the different amino acids like arginine, cysteine, histidine, lysine, methionine, tyrosine and tryptophane comprise 1/8, 1/9, 1/12, 1/24, 1/36 and 1/96 respectively of all the amino acid residues. On examining the ratio and the frequency of the different amino acids it is found that haemolysin molecule must contain at least 288 amino acid residues.

The minimum molecular weight of haemolysin as obtained by multiplying the number of amino acid residues by its average residue weight (115·2 g) is found to be 33,200.

The difference in molecular weight obtained by the two methods is thus about 4 per cent.

Bergmann and Niemann (*J. Biol. Chem.*, 1936, **115**, 77; 1937, **118**, 301; 1937, **122**, 577) have conducted a series of analysis of cattle haemoglobin, egg albumin, cattle fibrin and precursor of gelatin. It has been found by them that there exists a simple numerical relationship among the main amino-acids of these proteins. The total number of amino acid residues was deduced from the amino-acid composition of the protein by applying the periodicity hypothesis. It was found that cattle globulin contained 576 or $2^6 \times 3^2$ units, egg albumin 288 or $2^5 \times 3^2$ units and cattle fibrin 576 or $2^6 \times 3^2$ amino acid residues. From their results they have concluded that the total number of amino acid residues (N_t) and the number of individual amino-acid residues (N_i) and the frequency of the individual amino acid residues $(F_i = N_t/N_i)$ which are contained in a protein molecule can be expressed by the following equations:

(a) $N_t = 2^n \times 3^m$ where n and m are positive whole numbers.
(b) $N_i = 2^{n'} \times 3^{m'}$ where n' and m' are either zero or positive whole numbers.
(c) $F_i = 2^{n''} \times 3^{m''}$ where n'' and m'' are either zero or positive whole numbers.
(d) $n = n' + n''$.
(e) $m = m' + m''$.
(f) $Nt = Ni' + Ni'' + Ni''' + Nii' + \ldots\ldots\ldots\ldots\ldots + N_1{}^x$.

From the determination of the number of individual amino-acid residues and their respective frequencies the total number of amino-acid residues has been found. From the analysis of the above proteins it has also been concluded that genuine protein molecules contain $n \times 288$ units, where n is a whole number other than zero.

The same authors obtained the minimum molecular weight of cattle globulin, cattle fibrin and gelatin by multiplying the total number of amino-acid in the protein by its average residue weight. The average residue weight has been obtained by subtracting the molecular weight of water from the molecular weight, averaged with respect to amount of the amino acids recovered from acid hydrolysis. As the average residue weight of egg albumin was estimated to be 123·9, its molecular weight was found to be 35,700 ($123·9 \times 2^5 \times 3^2$) which is within the range of values (31,000 − 41,000) considered as the Svedberg unit. So also the molecular weight of cattle fibrin and cattle globulin were found to be 69,300 (*i.e.*, $120 \times 2^6 \times 3^2$) and 66,500 (*i.e.*, $115·5 \times 2^6 \times 3^2$) or equivalent to two Svedberg units.

As full theoretical recovery of the amino-acids has not been obtained after hydrolysis, the average was adjusted in favour of the amino acids of lower molecular weight, because these cannot be determined quantitatively. Moreover, the amount of carbohydrate, lipoid,

inorganic ions or prosthetic group must be known before the calculated molecular weight is compared with that obtained by physical methods.

The average residue weight has been estimated by determining by titration, the increase in the number of equivalents of carboxyl and amino plus imino groups obtained after hydrolysis by acid. From the increase in the number of equivalents of carboxyl or amino groups, the number of peptide bonds present in a given weight of protein can be determined. Consequently the average weight of protein or average residue weight containing one mole of peptide bond can be calculated. The method followed was that of Hotchkiss (*J. Biol. Chem.*, 1939, **131**, 387), which he applied in the case of lacto-globulin. The average peptide weight as estimated here is equal to the average residue weight as determined by Bergmann *et al* (*loc. cit.*), only when amino acids are the main constituents. As haemolysin has been found to contain only very small quantities of inorganic ions and carbohydrates, the above method has been considered suitable for determining the weight per peptide bond.

TABLE I

Ratio of amino-acids in haemolysin after hydrolysis

Amino-acids.	Mol wt.	Weight.	Gram mole per 100 g. protein	Ratio.	Frequency.
Arginine	174	18·94%	0·1088	36	8
Cysteine	121	11·60	0·0959	32	9
Histidine	155	11·25	0·0726	24	12
Lysine	146	5·24	0·0359	12	24
Methionine	149	3·62	0·0243	8	36
Tyrosine	181	4·34	0·0240	8	36
Tryptophane	204	1·81	0·0089	3	96

The percentage composition of crystalline haemolysin (De, *Ann. Biochem. Expt. Med.*, 1944, **4**, 45), has been determined for those amino acids for which reliable analytical methods are available and has been presented in column 2 of Table I. The values were recalculated on a gm. molecular basis and are given in column 3. The ratios of the amino acids given in column 4 were obtained from column 3. As the average residue weight of haemolysin is found to be 115·2 g., 100 g. of haemolysin must give approximately 0·868 g. molecule of the hypothetical average amino acid on complete hydrolysis. From the values given in column 3 it is observed that the various amino acids comprise 1/8, 1/9, 1/12, 1/24, 1/36, 1/36 and 1/96 of all the amino acid residues, and this frequency is given in column 5. On examining the ratios in column 4 and the fractional values in column 5, it can be concluded that haemolysin must contain at least 288 amino acid residues or a whole multiple thereof. When this number of amino acid residues is multiplied by the average residue weight (115·2), it is found that haemolysin has a minimum molecular weight of 33,200.

On analysis haemolysin was found to contain C, 48·66%, H, 6·21%, N, 15·92% and S, 3·88%.

The sulphur present in the form of cysteine and methionine accounts for the 3·85% of sulphur which is in fair agreement with the total sulphur content 3·88%. So it can be assumed that all the sulphur in haemolysin is present in the form of cysteine and methionine. The ultimate ratio of cysteine and methionine is found to be 32·8 (*vide*

column 4, Table I). So the minimum number of sulphur atoms present in haemolysin is 40. From this the ultimate composition of haemolysin has been found to be

$$C_{1347}H_{2063}O_{626}N_{375}S_{40}$$
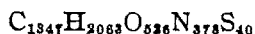
The minimum molecular weight of haemolysin from this ultimate composition is thus found to be 33,200. But the molecular weight determined by the diffusion method is 31,900. So the variation in molecular weight as determined by the two methods is not more than 6%.

Estimation of the Basic Amino-Acids.—The method employed for the determination of the basic amino-acids is that of Block (*J. Biol. Chem.*, 1934, **106**, 457) with slight modifications.

Estimation of Methionine and Cysteine.—The salt-free haemolysin was extracted with petroleum ether and dried in a vacuum desciccator over P_2O_5, since traces of alcohol interfere with the estimation of cysteine and methionine.

The method followed for the estimation of these two amino-acids is that of Baernstein (*J. Biol. Chem.*, 1936, **116**, 25, 33), as modified by Kassell *et al* (*ibid.*, 1938, **125**, 145).

Estimation of Tyrosine and Tryptophane.—The method employed is that of Folin and Marenzi (*J. Biol. Chem.*, 1929, **88**, 89).

Determination of Average residue weight.

Crystalline haemolysin (salt free 486 mg.) was boiled under reflux condenser in 15 c.c. of 6 N hydrochloric acid for 18 hours. The hydrolysate which contained no filtrable humin was made up to 50 c.c. From aliquot portions nitrogen and ammonia were determined. And a 40 c.c. portion was concentrated *in vacuo* three times for removing the major portion of hydrochloric acid. The residue was made up to 10 c.c. and from aliquot portions chloride and nitrogen were estimated. Increase in amino group was determined in 90% acetone solution by titration with 90% alcoholic 0·05 N hydrochloric acid using naphthyl red as indicator. Increase in carboxyl group was determined in 90% alcoholic solution by titration with 90 per cent alcoholic potassium hydroxide using thymolphthalein as indicator. The results recorded below are the average of three sets of experiments.

TABLE II

0·05N acid or alkali per mg. of nitrogen.

	Acid groups.	Basic groups.	Mean.
Groups in original protein	0·11 c.c.	0·13 c.c.	—
Groups in hydrolysed protein	1·32	1·32	—
Increase not corrected for ammonia (−NH$_2$ and −COOH groups)	1·21	1·19	1·20 c.c.
Ammonia	—	—	0·11
Peptide bond	—	—	1·09

From this the weight per peptide bond or average residue weight is found to be 115·2 g.

My best thanks are due to Dr. B. N. Ghosh for his kind encouragement and advice.

VARIATION OF THE DISSOCIATION CONSTANT OF A WEAK ACID BY SOLUBILITY METHOD

By A. P. Shitoot and W. V. Bhagwat

Variation of the dissociation constant of weak acids by solubility method has been investigated. The results are in accordance with the explanation given in previous papers by Bhagwat and co-workers.

It is observed by Bhagwat and Dhar (*J. Indian Chem. Soc.*, 1929, **6**, 807) and Bhagwat and Doosaj (*ibid.*, 1933, **10**, 477) that the dissociation constant of weak acids determined by solubility method varies with the concentration of the sodium or potassium salt taken for this purpose. The work is extended in this paper.

TABLE I

Dissociation constant of glycollic acid.

(i) With benzoic acid at $25.6°$. K_1 of benzoic acid at $30° = 6.4 \times 10^{-5}$. $a = 0.02864$.

(ii) With salicylic acid at $24.4°$. K_1 of salicylic acid at $30° = 1.6 \times 10^{-3}$. $a = 0.01545$.

c.	b.	$K_2 = K_1.a.(c-b+a)/(b-a)^2$.	c	b.	$K_2 = K_1.a.(c-b+a)/(b-a)^2$.
0.00514	0.03114	7.7×10^{-4}	0.00964	0.02341	6.5×10^{-4}
0.01456	0.03454	4.5	0.02892	0.03682	4.1
0.02892	0.04023	2.3	0.03856	0.04136	4.6
0.03856	0.04250	2.3	0.05785	0.05500	2.9
0.05785	0.04818	1.0	0.1157	0.08137	2.7
0.1157	0.05819	1.6			
0.2315	0.07364	1.7			

The dissociation constant of glycollic acid is 1.5×10^{-4}. The results are of the same order of magnitude. At low concentration the results are high but they decrease with the increase of concentration of the potassium salt and approach the required value.

The results with salicylic acid are similar although in general they are higher than those obtained with benzoic acid.

TABLE II

Dissociation constant of lactic acid.

(i) With benzoic acid at $26°$.
K_1 of benzoic at $30° = 6.4 \times 10^{-5}$.
$a = 0.02909$.

(ii) With salicylic acid at $24.7°$.
K_1 of salicylic acid at $30° = 1.6 \times 10^{-3}$.
$a = 0.01568$.

c.	b.	$K_2 = K_1.a.(c-b+a)/(b-a)^2$.	c.	b.	$K_2 = K_1.a.(c-b+a)/(b-a)^2$.
0.00438	0.03159	5.6×10^{-4}	0.02466	0.03363	5.2×10^{-4}
0.00548	0.03250	3.3	0.03288	0.03909	3.5
0.00822	0.03318	4.6	0.04932	0.04909	3.1
0.01233	0.03523	3.0	0.09865	0.07409	2.9
0.02466	0.04091	1.7	0.1973	0.1150	2.5
0.03288	0.04228	2.1			
0.04932	0.04681	1.8			
0.09865	0.05728	1.6			
0.1973	0.07046	1.7			

Dissociation constant of lactic acid is $1·4 \times 10^{-4}$. The values obtained with benzoic acid are of the same order of magnitude and approach it more nearly as the concentration is increased. The values are high at low concentrations but fall gradually as the concentration of the salt is increased.

The results obtained with salicylic acid are very similar although the values in general are of a higher order of magnitude than those obtained with benzoic acid.

<div align="center">TABLE III</div>

<div align="center">*Dissociation constant of n-butyric acid.*</div>

(i) With benzoic acid at $25·9°$.   (ii) With salicylic acid at $25·2°$.

    K_1 of benzoic acid at $30° = 6·4 \times 10^{-5}$. K_1 of salicylic acid at $30° = 1·6 \times 10^{-3}$.

            $a = 0·02904.$ $a = 0·01608.$

$c.$	$b.$	$K_2 = K_1.a.(c-b+a)/(b-a)^2.$	$c.$	$b.$	$K_2 = K_1.a.(c-b+a)/(b-a)^2.$
0·00772	0·03544	$6·0 \times 10^{-5}$	0·01688	0·03097	$2·3 \times 10^{-5}$
0·01080	0·03872	2·2	0·03377	0·04677	8·4
0·01801	0·04527	1·0	0·04503	0·05689	6·5
0·03377	0·05719	1·3	0·06755	0·07727	4·3
0·04503	0·06494	1·3	0·1351	0·1379	2·3
0·06755	0·07923	1·3	0·2702	0·2478	1·8
0·1351	0·1161	1·2			
0·2702	0·1716	1·2			

The dissociation constant of butyric acid is about $1·5 \times 10^{-5}$. The values therefore approach this limit for higher concentrations. For low concentrations the values are high.

The salicylic acid is stronger than benzoic acid and as such given values are greater than those obtained by using benzoic acid. At low concentration the dissociation constant is high while it falls with increased concentration of potassium salt.

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SOME COMPLEX COMPOUNDS OF BENZENE WITH SULPHUR, IODINE, ETC.

BY BHOLANATH GHOSH AND SUDARSAN PROSAD SINHA

Mechanism of the formation, association and dissociation of the complexes formed between benzene and sulphur or iodine has been investigated from a study of their absorption spectra.

The electrical conductivity of the benzene solution of sulphur or iodine exhibits breaks at 0·54, 0·78 and 1·41% of S and at 0·10, 0·14 and 0·21% of I_2. This brings out the fact that the type of complexes unearthed by the study of the microscopic Raman effect are real. The increase of the conductivity of benzene on the addition of sulphur or iodine shows that some degree of ionisation has been induced therein by these solutes. The purpose of this note is to study the mechanism of the formation, association or dissociation of these complexes ·from a study of their absorption spectra. The complexes mentioned here may be of the same type as met with in the case of the formation of "lakes" by dyestuff with inorganic salts.

EXPERIMENTAL

The light from a hydrogen continuum was passed through the benzene or benzene solutions placed in a quartz tube and the photographs of the absorption spectra were taken on panchromatic plates with a Hilger E_1 quartz spectrograph.

The position of the absorption maxima (m) and the absorption edges (e) are given in Table I.

TABLE I

Temp. 40°.

Absorber.	Absorption edge.	Absorption maxima.	Absorber.	Absorption edge.	Absorption maxima.
Benzene	5852Å	5250Å	Benzene+0·2%I	5760Å	5250Å
	3260	3180		3960	3930
	3080	3020	Benzene+0·5%S	5810	5010
	2860	2810	+0·15%I	3880	3820
Benzene+0·28%S	5842	5210	Benzene+0·5%S	5700	5012
	3700	3620	+0·15%I+FeCl₃(10%	3920	3860
Benzene+0·52%S	5790	5240	aqueous solution)20%·	2890	2830
	3780	3910	Benzene+·5%S	4510	4420
Benzene+1·2%S	5770	5260	+·1%I+KCl(10%	3980	3860
	3800	3960	aqueous solution)15%	2840	2800
Benzene+0·1%I	5800	5220			
	3980	3920			

DISCUSSION

The strength of the bonds in the benzene .complexes is indeed small, so that the absorption of light in the red region of the spectrum easily brings about their dissociation. For benzene and 0·10% of I_2, λ less than 5800Å brings about the rupture of the bonds

between the constituents of the complexes. This leads to a value of the heat of dissociation equal to R, where

$$R = \frac{Nh\nu}{J} = \frac{286,000}{\lambda(\text{Å})} = 49\cdot31 \text{ kilo-calories.}$$

Here h is Plank's constant, N is Avogadro's number, ν, the frequency of the quanta and J, the Joule's equivalent. The retransmitted patch below 5220Å shows that the absorption of light above the corresponding frequency, not only dissociates the complex, but also raises iodine normal or ionised to higher states of electronic excitation. Such a phenomenon is met with in the case of photodissociation of diatomic molecules. The photodissociation at λ 5800Å disrupts the constituents into normal states, while the photodissociation at 3980Å after breaking asunder the complex raises the constituents, one or both to higher excited states and these ruptured parts then fly apart with the balance of energy shared as kinetic energy between them. The difference of frequency corresponding to the shift of the position of absorption from ν 25125 to 17241 cm^{-1} comes out to be 7884 cm^{-1}, while the frequency difference for the states $6d^3D_1$ and $6d^3D_3$ of I^+ is 8372 cm^{-1}. The agreement between these values is nice, and it involves a forbidden transition. The phenomenon of the collision of the first and the second kind, as well as the regular and forbidden transitions play a significant rôle in the thermal or photochemical dissociation of these complexes which become heavier on further addition of S, I, $FeCl_3$ or KCl.

Coming to the sulphur complexes of benzene, we find that the dissociation begins at 5840Å. Hence the heat of dissociation is 48·96 K. calories. The frequency difference between the two important edges of this complex is $27027 - 19194$ cm^{-1} i.e., 7833 cm^{-1} and a second difference is $27624 - 19194 = 8430$ cm^{-1}. These differences agree well with $\nu = 9672$ cm^{-1}, involving the transition $3s^2 3p^3{}^2D_{\frac{3}{2}}$ and $3s^2 3p^3{}^2P_{\frac{1}{2}}$ of S^+, showing that the nature of these complexes is ionic in character and Kratzer's theory of the dissociation of diatomic molecules as modified by Born and Frank ($Z.$ $Physik$, 1925. **31**, 1411) may be applicable to the photodissociation of these complexes.

We express here our sincere thanks to Professors S. P. Prosad and D. K. Bhattacharya for their kind interest in this work.

PHYSICS DEPARTMENT, SCIENCE COLLEGE, PATNA.   *Received April 25, 1944.*

THE VAPOUR PRESSURE OF SOME STABLE AND UNSTABLE HYDRATES

By Bholanath Ghosh

Vapour pressures of a number of stable and unstable hydrates have been determined by analytical method by absorbing the vapour in H_2SO_4 and determining the strength of the acid afterwards.

The author has been able to detect the presence of a large number of unstable hydrates by the differential thermo E. M. F. method (*J. Indian Chem. Soc.*, 1943, 20, 121). He has further observed that the life of these transient hydrates gets frozen when intimately mixed with some catalysers. The purpose of the present paper is to report on the vapour pressure of the stable and unstable hydrates, when the experiment is performed in a vibration-free environment.

EXPERIMENTAL

The hydrate, whose vapour pressure is required, is placed in one limb of an inverted U-tube and in the other limb concentrated sulphuric acid is kept. The tube is then evacuated and sealed. The whole arrangement is kept in a thermostat at a known temperature for 1 to 10 days. Water molecules from the hydrates distil off to the H_2SO_4, till the vapour pressure of the mixture of H_2O and H_2SO_4 equals that of the hydrate; when further distillation stops. By titration of the H_2SO_4 solution after the experiment is over, its strength is determined and hence its equilibrium vapour pressure.

The characteristic hydrates were prepared by keeping the samples at the temperatures at which they are formed for one day and then they were carefully removed to the experimental tube in such a way that they did not absorb moisture in the process. In the case of $CuSO_4$ the temperature of the thermostat was 35° and in the case of $BeSO_4$, 14°. In some cases, the above arrangement was connected to a capillary oil manometer and the vapour pressure read directly. Here also H_2SO_4 acted as an absorbent of the evolved water molecules.

The fact that the hydrates have the characteristic composition as published in the previous paper at a particular temperature after they have remained in the thermostat for a long time was also checked by the determination of the percentage of the cationic radical in the final sample of the hydrate.

RESULTS

The data obtained are given in Table I, where x represents the number of molecules of H_2O in the hydrate and p is the vapour pressure in mm. of Hg.

Evidently from the figure the hydrates reported are genuine as shown by the vapour pressure measurement. The equilibrium value of the vapour pressure comes with extreme slowness and sometimes the samples are to be kept in the thermostat for 8 to 10 days before measurements can be relied on. This point is also borne out by the work of Patrick and McGovan (*J. Amer. Chem. Soc.*, 1920, 42, 946).

TABLE I

	Stable hydrates.		Unstable hydrates.			Stable hydrates.		Unstable hydrates.	
	x	p	x	p		x	p	x	p
CuSO₄ mixed with silica	1	0·21	4⅓	15·42	BeSO₄ mixed with silica	1	0·11	1½	0·31
powder at 35°	2	3·42	4½	16·11	powder at 14°	2	0 62	4⅓	5·11
	3	11·22	—	—		3	1·21	—	—
	4	14·13	—	—		4	3·84	—	—
	5	17·41	—	—		5	6·23	—	—
CuSO₄ in presence of gold	1	0·28	4⅓	15·51	BeSO₄ mixed with sodium	1	0·08	¼	0·03
dust at 35°	2	3·49	—	—	silicate	2	0·54	—	—
	3	12·00	4½	16·23		3	1·19	1½	0·29
	4	14·02	—	—		4	3·52	—	—
	5	16·83	—	—		5	6·11	4¾	4 82

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FURTHER CHEMICAL EVIDENCES REGARDING THE RELATIVE POSITION OF DOUBLE BOND AND KETO GROUP IN ARTOSTENONE

By M. C. Nath and M. K. Chakraborty

A new derivative of artostenone,—dihydroxy-artostenone—has been prepared, the formation of which, according to Butenandt gives additional support to the view that artostenone is an $\alpha\beta$-unsaturated ketone. 2 : 4-Di-nitrophenylhydrazone of artostenone has also been prepared.

The structure of artostenone (I), the steroid ketone isolated from the unsaponifiable matter of the latex of Indian summer fruit *Artocarpous integrifolia*, has been based on chemical as well as X-ray data, previously presented (Nath, *Z. Physiol. Chem.*, 1937, **247**, 16 ; **249**, 71, 78; Nath and Mukherjee, *J. Indian Chem. Soc.*, 1939, **16**, 229). Butenandt *et al* (*Ber.*, 1938, **71B**, 1483) have shown that cholestenone, an $\alpha\beta$-unsaturated ketone, undergoes oxidation with hydrogen peroxide in presence of osmic acid and forms dihydroxycholestanone. Applying the same reaction artostenone is converted into dihydroxy·artostenone (II), though hydrogen peroxide alone has got no action on the former. Petro and Starling (*J. Chem. Soc.*, 1940, 60) have recently shown that Δ^5-cholestene-3 : 4-dione, an $\alpha\beta$-unsaturated ketone, forms 2 : 4-dinitrophenylhydrazone with Bredig's reagent (2 : 4-dinitrophenylhydrazine). By application of the same method a corresponding derivative of artostenone has also been prepared.
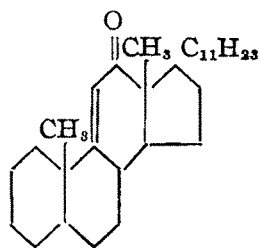
(I)
Artostenone.
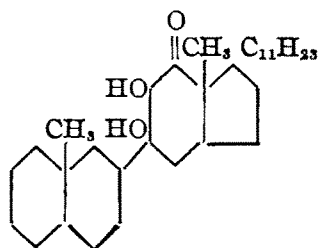
(II)
Dihydroxy-artostenone.

Experimental

Preparation of Dihydroxyartostenone.—Artostenone (2 g.) was dissolved in ether (100 c.c.) and treated with osmic acid (0·1 g.) in 10 c.c. of ether. 30 C.c. of perhydrol were then added to the mixture and the latter was allowed to remain for 20 hours at ordinary temperature. The resulting solution was then evaporated completely and·dried without application of heat, until the odour of osmic acid was removed. It was once again dissolved in ether and decolourised with 1 or 2 drops of perhydrol and evaporated. The colourless semicrystalline residue (1·8 g.) after several crystallisation gave a beautiful 6-sided crystalline substance (0·4 g.) m.p., 141-42°. (Found : C, 78·32 ; H, 11·27. $C_{30}H_{52}O_3$ requires C, 78·26 ; H, 11·30 per cent).

·*Acetate of Dihydroxyartostenone.*—Dihydroxyartostenone (0·05 g.) was dissolved in a few drops of pyridine and refluxed for 12 minutes on a sand-bath with a few drops of acetic anhydride. It was then cooled, poured into water and extracted with ether; ether was evaporated off and the residue crystallised several times from methyl alcohol,

m.p. 89-90°. (Found : C, 74·91; H, 10·32. C₃₄H₅₆O₅ requires C, 75·0, H, 10·29 per cent).

Oxime of Dihydroxyartostenone.—An alcoholic solution of dihydroxyartostenone (0·1 g.) and 0·05 g. of hydroxylamine hydrochloride and an excess of sodium acetate was refluxed for 15 minutes on a water-bath, cooled, diluted with water and shaken with ether in a separating funnel. The ethereal layer was separated and ether evaporated off. The solid residue was crystallised repeatedly from absolute alcohol as needles, m.p. 215-16°. (Found : N, 2·88. C₃₀H₅₃O₃N requires N, 2·94 per cent).

The Semicarbazone.—An alcoholic solution of dihydroxyartostenone and an aqueous alcoholic solution of semicarbazide hydrochloride and an excess of sodium acetate were refluxed for 6 hours on a water-bath, cooled and poured into water. The precipitate was filtered, washed repeatedly with water and finally crystallised from alcohol, m.p. 178-80ᶜ. (Found : C, 71·88 ; H, 10·70. C₃₁H₅₅O₃N₃ requires C, 71·95 ; H, 10·63 per cent).

The 2 : 4-Dinitrophenylhydrazone of Artostenone.—An alcoholic solution of artostenone (0·2 g.) and of 2 : 4-dinitrophenylhydrazine (0·2 g.) was boiled with a few drops of concentrated hydrochloric acid, when 2 : 4-dinitrophenylhydrazone of artostenone was precipitated. It was filtered, washed and dried. The total yield was 0·32 g. It was crystallised from benzene-alcohol mixture (4 : 1) as flowery orange red crystals, m.p. 228-29°. (Found : N, 9·05. C₃₆H₅₄O₄N₄ requires N, 9·24 per cent).

Our best thanks are due to Prof. J. K. Chowdhury for his kind interest in the work.

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m.p. 89-90°. (Found : C, 74·91; H, 10·32. $C_{34}H_{56}O_5$ requires C, 75·0, H, 10·29 per cent).

JCU 911

THE ABSORPTION SPECTRA OF CHROMIUM AND COBALT CHLORIDE

By BHOLANATH GHOSH

P22 769

The absorption maxima of the aqueous solutions of $CrCl_3$ and $CoCl_2$ have been measured, in or without the presence of the added impurities of KCl or Cl_2 and also in presence of electric and magnetic fields. Judging from the agreement of the values of wave numbers of these maxima with the term differences of the relevant ions, it is concluded that in the aqueous solutions both singly and multiply charged ions exist in equilibrium and this state is disturbed by the presence of the electric and magnetic fields and also by the addition of impurities. The shifts of the position of the bands arising from the different types of changes of environment round the ions are also recorded.

The problem of the colour of the inorganic salts have not as yet been solved in a satisfactory manner. The salts in solution generally possess the same colour as in crystals. Joos (*Ann. Physik*, 1926, **11**, 1076) explains that the colour formation arises from aqua-complexes. Saha (*Bull. Acad. Sci. U. P.*, 1931, **1**, 1) traces the origin of colour in the dissolved free ions, because he finds that the frequency difference between two absorption maxima coincides with the term difference of two deepest levels of the ions Kato (*Sci. Inst. Phys. Chem. Res. Japan*, 1930, **13**, 232), Bose (*Z. Physik*, 1933, **18**, 361, 376), and Karim and Samuel (*Bull. Acad. Sci. U. P.*, 1934, **3**, 157) also hold the same view. From a study of the absorption maxima of aqueous solutions of $CrCl_3.6H_2O$ Karim and Samuel opine that the ions Cr^{+3}, Cr^{-2} and Cr^{+} co-exist simultaneously in the solvated condition in the solution. Bose and Mukherji (*Phil. Mag.*, 1938, **26**, 757 ; *Indian J. Phys.*, 1939, **13**, 219) have applied Van Vleck's theory to explain the formation of the absorption spectra of paramagnetic salts or their complexes. The purpose of the present paper is to see how the position of the absorption bands change with the temperature, with the addition of minute traces of impurities and also under the application of the electric and magnetic fields.

EXPERIMENTAL

The spectrophotometer, described by the author elsewhere (*Current Sci.*, 1941, **10**, 325) was used for this investigation in the visible region. The white light from a point-o-lite, after passing through the cell falls on the upper split-slit of a Hilger constant deviation spectrometer. Below this slit there is another half-slit, in the same vertical line, on which the light from a tungsten filament lamp could be projected with the help of a totally reflecting prism. The width of the lower slit was varied by a calibrated screw-head containing fine graduations and hence the intensity of the lower beam was adjusted to any arbitrary value. A small strip of the same range of wave-length from both spectra is sorted out by a slit in the field of view of the observing telescope and matched. Two cells of different thickness were used for the determination of the extinction coefficient. The temperature of the cell was varied by putting it in an air thermostat, having proper holes for the passage of light. For the ultraviolet region the method of photographic photometry was adopted using a hydrogen continuum as a source. A series of intensity marks were given by altering the width of the slit in the ratio 1 : 8 : 40 : 100. The time of exposure of the intensity marks and the absorption spectra were kept the same. The intensity of the light passing through the step-slit was varied by putting neutral ground glass filters in the path of the beam. The plates were microphotometered with a Zeiss recording microphotometer and the photographic density of the spectra and the calibrating marks were determined at various wave-lengths.

For applying the magnetic field the cell was placed in between the parallel pieces of a large electromagnet, where field upto 30,000 Gauss could be produced. For applying the electric field the cell was put between two parallel plates 10 cm. apart. Direct electric field of 40 K. V. per cm. is applied between them from a transformer using a mechanical rectifier, as used with an X-ray plant. The light travelled as a parallel beam through the cell in the electric or magnetic field, perpendicular to the lines of forces.

The data obtained with the aqueous solution of $CrCl_3$ and $CoCl_2$ under various conditions are given in Table I. The strength of the $CrCl_3$ solution was $1/50N$ and that of $CoCl_2$ $1/10$ N.

TABLE I

Solution.	Added salt or element.	Temp.	Electric or magnetic field.	1st.	2nd.	3rd.	4th.	5th.	6th.	Strength of the added salt or element.
CrCl₃	—	24·1	—	670	608	583	516	440	308	
N/50	—	54·2	—	685	620	596	530	445	320	
	—	95·0	—	698	634	606	545	442	310	
	Cl₂	25·0	—	652	582	564	524	450	301	N/1000
	Cl₂	25·0	—	644	564	550	524	446	294	N/240
	KCl	25·0	—	684	620	595	520	447	315	N/1000
	—	26·0	H = 25000 Gauss	662	593	565	508	438	362,336	
	—	25·8	E = 5K.V. per cm.	662	571	543	441	312	222	
CoCl₂	—	23·2	—	562	501	432	320			
N/10	—	55·0	—	572	521	448	322			
	—	94·0	—	584	532	457	321			
	Cl₂	26·0	—	550	486	412	318			N/400
	Cl₂	25·0	—	541	475	401	306			N/100
	KCl	27·2	—	552	489	422	323			N/3000
	—	25·8	H = 25000 Gauss	575	485	455	410			
	—	26·2	E = 5K.V. per cm.	560	472	420	310	318		

DISCUSSION

The effect of increasing temperature is to shift the position of the bands to regions of longer wave-length. It is possible that all the ions in solutions exist in a loosely hydrated condition and that some part of the thermal energy is used up in breaking assunder these weak hydration bonds, before they are raised to states of higher quantum energy. The increasing temperature supplies greater thermal energy to these loose complexes helping their thermal disruption and hence the photonic energy subtracted from the continuum becomes less. This is why on increasing the temperature the degree of hydration becomes less.

The addition of KCl and Cl_2 shifts some of the bands towards the ultraviolet and others towards the red region.

The absorption bands are related to the term difference of the ions as described in the introduction.

In the case of $CrCl_3$, the magnetic field shifts all the bands towards the ultraviolet, excepting the band at 308 mμ, which is shifted towards the red and is broken into two components 362 and 336 mμ. For $CoCl_2$ the band 562 mμ is shifted to 575 mμ; 501 to 485 mμ. The absorption maximum 432 mμ is broken into two components 455 and 410 mμ; and the maximum 320 goes to 318 mμ.

The electric field shifts all the bands of $CrCl_3$ towards the ultraviolet very distinctly. For $CoCl_2$ also, the displacements of the bands are in the same sense, but the shifts are not so characteristic. The explanation of these shifts is difficult and more data are necessary before any theory can be built up explaining their origin.

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EFFECT OF AGEING ON THE VISCOSITY OF SOLS

By S. D. JHA AND S. GHOSH

The effect of ageing on the sols of stannic hydroxide, ferric phosphate and vanadium pentoxide of different purities and dilutions, at variable shearing forces have been studied, in this paper. The conclusions have been as follows :—(i) the viscosity of a concentrated sol increases on ageing and reaches a maximum value, which is followed by a decrease; (ii) the viscosity of a dilute sol decreases at first and then there is an increase followed by a decrease; (iii) the purer the sample, sooner the ageing takes place; (iv) the more dilute the sample, sooner the ageing takes place; (v) changes in the viscosity of a sol with ageing are more pronounced with concentrated sols than with dilute ones; (vi) higher the pressure, lower are the changes in viscosity of a sol with ageing.

The changes of viscosity on the ageing of sols have been investigated by number of workers. The results presented in this paper on the measurement of viscosities for the sols of stannic hydroxide, ferric phosphate and vanadium pentoxide obtained at their various stages of dialysis, and different dilutions, carried out at variable shearing forces, lead to the conclusion that the effect of ageing on the viscosity of the sols is intimately related with the purity and concentration of the sols. The concentrated sols, which are capable of developing the structural flow prominently, usually show an increase in the viscosity to a maximum with age.

In a number of communications Dhar and Chakravarty (*Kolloid Z.*, 1927, **42**, 149 ; *Z. anorg. Chem.*, 1927, **168**, 209) have reported the influence of ageing on the viscosities of both organic and inorganic colloids and these authors have concluded that in general lyophilic colloids show an increase whilst the lyophobic ones are characterised by developing a decrease in their viscosities with time. This behaviour of the two types of colloids has been ascribed to the difference in the hydration of the colloids with age. Desai and co-workers (*Trans. Nat. Inst. Sci. India*, 1939, **2**, ii) emphasize the considerable change in the physical properties of colloids on dialysis. It is also well known that the concentration of the sols remarkably affects their physical properties. In this paper we have therefore investigated the effect of age on viscosity of some sols of different purities and concentrations.

EXPERIMENTAL

The viscosity of the sols have been determined by an apparatus, similar to that of Farrow and Ostwald, and modified by Ayub and Ghosh (*Bull. Acad. Sci.*, 1939, **9**, 149). The relative viscosity of the sols are given by

$$\frac{\eta_s}{\eta_w} = \frac{1/t_1 + 1/t_2}{1/t_1' + 1/t_2'}$$

where η_s is the viscosity of the sol at a definite temperature and pressure, and η_w is the vtscosity of water under the same conditions, t_1 and t_2 represent the time of flow downwards and upwards the tube for water and t_1' and t_2' are the corresponding times for the sols. The accuracy of this apparatus has been described in a previous paper.

Stannic Hydroxide Sol

This sol was prepared by peptising a well washed stannic hydroxide precipitate by concentrated ammonia, which was removed to different amounts by dialysis carried out at different stages in cold. The various samples of sol at different stages of purities (A, A', A'', A''',) were taken out and diluted to their one-third and one-ninth concentration,

All these sols were stocked in glass-stoppered Jena bottles and their purities were determined from the ammonium radical present in the sols in the usual way. The results obtained for 23 c.c. of these sols mostly at a pressure of 30 cm. of water column, and temperature 30° are recorded below. In some cases the results of the measurement of viscosity at different shearing forces (care being taken to avoid turbulent flow) are also given.

TABLE I

Conc. of sol A = 45·16 g./l. of solid matter.
Conc. of $NH_4^+ = 1·36$ g./l.

Time.	Sol A.	Sol A/3.	Sol A/9.
0 days	1·1000	1·016	1·000
7	1·1207	1·013	1·000
20	1·1417	1·036	1·000
45	1·1478	1·041	1·023
61	1·1511	1·015	1·031
103	1·1650	1·000	1·000

TABLE II

Conc. of the sol A' = 42·40 g./l. of solid matter.   Conc. of $NH_4^+ = 0·823$ g./l.

Time.	Sol A'.	Sol A'/3.	Sol A'/9.
0 days	1·138	1·044	1·021
6	1·142	1·040	1·020
19	1·149	1·055	1·023
44	1·153	1·029	1·021
59	1·166	1·023	1·021
102	1·540	1·019	1·011

TABLE III

Conc. of the sol A″ = 36·58 g./l. of solid matter. Conc. of $NH_4^+ = 0·501$ g./l.

Time.	Sol A″.	Sol A″/3.	Sol A″/9.
0 days	1·189	1·057	1·023
14	1·199	1·024	1·015
21	1·214	1·055	1·027
43	1·205	1·058	1·030
57	1·205	1·049	1·011
99	1·192	1·029	1·005

TABLE IV

Conc. of Sol A‴ = 39·92 g./l. of solid-matter. Conc. of $NH_4^+ = 0·295$ g./l.

Time.	Sol A‴.	Sol A‴/3.	Sol A‴/9.
0 days	1·206	1·068	1·033
10	1·230	1·064	1·030
21	1·243	1·058	1·040
42	1·246	1·067	1·053
45	1·204	1·052	1·041
90	1·191	1·038	1·014

TABLE V

$\frac{\eta_s}{\eta_w}$ of sol A at different pressures of water column in cm.

Time.	30 cm.	45 cm.
0 days	1·1000	1·088
7	1·1207	1·103
20	1·1417	1·114
45	1.1478	1·115
62	1·1511	1·122
104	1·1650	1·147

Ferric Phosphate Sol

The ferric phosphate sol was prepared by the interaction of ferric chloride and potassium dihydrogen phosphate. The sol thus obtained was dialysed to different extents, and the samples taken out at different stages of purity, which is estimated from the amounts of chloride radical per litre. Different samples were designated as B, B', B″, B‴. As before the volume of the sol taken was 23 c.c., pressure = 30 cm. of water and temperature = 30°.

TABLE VI

Conc. of the sol B = 51·52 g./l. of solid matter. Conc. of Cl′ ion = 0·236 g. ion/l.

Time.	Sol B.	Sol B/3.	Sol B/9.
0 days	1·120	1·029	1·011
12	1·120	1·023	1·009
33	1·148	1·019	1·000
50	1·153	1·014	1·000
65	1·163	1·009	1·000

TABLE VII

Conc. of the sol B' = 51·52 g./l. of solid matter.   Conc. of Cl′ ion = 0·2360 g. ion/l.

Time.	Sol B'.	Sol B'/3.	Sol B'/9.
0 days	1·149	1·053	1·021
10	1·137	1·053	1·005
21	1·153	1·032	1·000
41	1·163	1·039	1·045
50	1·174	1·042	1·063

TABLE VIII

Conc. of the sol B″ = 34·67 g./l. of solid matter. Conc. of Cl′ ion = 0·0047 g. ion/l.

Time.	Sol B″.	Sol B″/3.	Sol B″/9
0 days	1·271	1·076	1·029
7	1·285	1·053	1·013
28	1·313	1·052	1·000
45	1·406	1·069	1·000
61	1·575	1·028	1·000

TABLE IX

Conc. of the sol B''' = 31·63 g./l. of solid matter. Conc. of Cl' = 0·0022 g. ion/l.

Time.	Sol B'''.	Sol B'''/3.	Sol B'''/9.
0 days	1·428	1·108	1·041
5	1·547	1·096	1 007
26	1·561	1·101	1·073
49	1·563	1·101	1·039
58	1·566	1·068	1·034

TABLE X

$\frac{\eta_s}{\eta_w}$ of sol B'' at different pressures of water column in cm.

Time.	30 cm.	45 cm.
0 days	1·271	1·245
7	1·285	1·276
28	1·313	1·306
45	1·406	1·343
61	1·575	1·538

Vanadium Pentoxide Sol.

The sol was prepared by treating ammonium vanadate with concentrated HCl, in a pestle and mortar and mixed thoroughly till it became deep blood red. This precipitate of vanadium pentoxide was washed on a filter paper with distilled water, when the precipitate showed the tendency to peptisation. The whole precipitate was thoroughly shaken with an excess of water and the sol kept in a parchment paper for cold dialysis. Various samples were taken out at different stages of purity and designated as C, C', C'', C'''. As before the experiments were conducted with 23 c.c. of the sol at a pressure of 30 cm. of water and at 30°.

TABLE XI

Conc. of sol C = 12·012 g. of V$_2$O$_5$ per litre.

Time.	Sol C.	Sol C/3.	Sol C/9.
0 days	1·123	1·032	1·016
12	1·142	1·050	1·019
26	1·150	1·051	1·019
52	1·204	1·050	1·019
70	1·239	1·043	1·000

TABLE XII

Conc. of sol C' = 11·466 g. of V$_2$O$_5$ per litre.

Time.	Sol C'.	Sol C'/3.	Sol'/9.
0 days	1·136	1·047	1·021
10	1·152	1·030	1·015
24	1·163	1·036	1·030
50	·1·171	1·043	1·032
68	1·215	1·040	1·030

TABLE XIII

Conc. of the sol C'' = 10·556 g. of V$_2$O$_5$ per litre.

Time.	Sol C''.	Sol C''/3.	Sol C''/9.
0 days	1·139	1·054	1·012
8	1·145	1·042	1·008
22	1·153	1·046	1·038
47	1·157	1·048	1·040
65	1·192	1·045	1·000

TABLE XIV

Conc. of the sol C''' = 9·828 g. of V$_2$O$_5$ per litre.

Time.	Sol C'''.	Sol C'''/3.	Sol C'''/9.
0 days	1·147	1·049	1·020
5	1·155	1·036	1 007
22	1·163	1·047	1·020
47	1·170	1·048	1·020
65	1·127	1·041	1·013

TABLE XV

$\frac{\eta_s}{\eta_w}$ of sol C'' at different pressure of water column in cm.

Time.	20 cm.	30 cm.	95 cm.
0 days	1·139	1·134	1·116
8	1·162	1·145	1·124
22	1·168	1·153	1·126
47	1·175	1·157	1·126
65	1·220	1·192	1·137

DISCUSSION

One of the properties of colloids affected by ageing of the sols is their viscosity. Our results have shown that in general the changes in the viscosities of these sols have been more prominent in the case of the concentrated sols than in the case of dilute ones. The viscosities of the pure concentrated sols of stannic hydroxide, ferric phosphate and the purest sample of vanadium pentoxide have a general tendency to increase with time. In some cases within a period of two to three months of observation, there is definite evidence of a tendency to decrease, for the viscosities of these sols, after they have attained the

maximum value. Similar changes in the viscosity of a sol of ceric hydroxide were recorded by Chakravarti, Ghosh and Dhar (cf. "Colloid Chemistry" by J. Alexander, Vol. II, p. 105). Davies, Oakes and Browne (J. Amer. Chem. Soc., 1921, **43**, 1526) also report that the viscosity of gelatine solution increases with time, and reaches a maximum in about twenty four hours, higher grades of gelatine-may show greater increase in viscosity. In this connection it should be stated that this increase in viscosity to its maximum is more quickly attained for dilute and pure sols than for concentrated and impure sols. Thus in the case of the first three impure sols of vanadium pentoxide, the maximum increase in viscosity was not observed even in two and a half months of observation, and a decrease in the viscosity, from the maximum value for the concentrated sol was noted only with the purest sample of vanadium pentoxide.

In accordance with the views developed by Chakravarti and Dhar (loc. cit.) on the viscosity of sols, it may be suggested that with ageing the hydration of the colloid particles increases, reaches a maximum and then decreases owing to agglomeration of the particles, which results in a subsequent decrease in the viscosity. It will however be seen from Tables V, X and XV that the variations in the viscosity of these sols are more remarkable for measurements carried out at low pressures than at the higher ones. It may be therefore suggested that these variations of viscosities of the sols are intimately connected with the structure that is usually associated with the colloid particles of hydrated sols. It is possible that the increase in the viscosities of these sols on ageing in the earlier stages of the process is more due to this structure formation than due to the slight changes in the hydration of the colloid particles. Ghosh and co-workers (Bull. Acad. Sci. U. P. 1939) have emphasised the prominence of the structure flow for concentrated and pure sols, and hence this behaviour of the changes in viscosity on ageing is likely to be observed more with these sols than with dilute and impure ones.

It may be noted that for the dilute sols, though the variations in the viscosities with time are much less than for the concentrated ones, yet their behaviour is quite significant. For dilute sols, it has been generally found that there is first a decrease, and then an increase followed by a continuous fall in the viscosity with time. These results can be explained on the view already stated that in the case of the dilute sols, the structural flow being much less prominent, these sols first show the ordinary tendency to decrease in viscosity with age. When however these dilute sols have become considerably unstable on ageing (as will be shown in a subsequent paper) these sols may develop the structural flow and be similar in behaviour to the concentrated ones, showing an increase in viscosity followed by a decrease.

It may therefore be concluded that sols in general have a tendency to decrease in viscosity with age, either because of a lesser degree of hydration or due to Smoluchowski's electro-viscous effect due to the decrease in electric charge on colloidal particles with time. If however the sol is of a character that develops structural flow, as is usually true for highly viscous sols, it may show an increase in viscosity to a maximum and then a decrease with age. In the case of concentrated sols or such sols as contain some of the substances in true molecular species, developing the structural flow the time for observing the decrease in the viscosity of the sols may be long, as in the case with impure vanadium pentoxide sols.

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A NOTE ON THE STABILITY OF SOME SUBSTITUTED SEMICARBAZIDES

By T. N. Ghosh

Recently Baker and Gilbert (*J. Amer. Chem. Soc*, 1942, **64**, 2777) have studied the kinetics of the transformation of hydrazine cyanate into semicarbazide and also of the conversion of semicarbazide into hydrazine cyanate. They have found that increase in ionic strength reduces the velocity of reaction in a manner which agrees with the postulate that the rate determining process is the reaction between the hydrazine and cyanate ions. It has now been considered worth while to make a comparative study of the stability of some substituted semicarbazides.

When 1-*o*-nitrophenylsemicarbazide (Guha and Ghosh, *J. Indian Chem. Soc.*, 1928, **8**, 441) is heated with aniline at 140-150°, carbanilide is obtained. Similarly, sym-di-*p*-tolylurea is obtained if *p*-toluidine is used in place of aniline. This formation of carbanilide or sym-di-*p*-tolylurea is evidently due to the interaction of aniline or *p*-toluidine with *iso*cyanic acid (HNCO), the latter having been formed by the pyrolysis of 1-*o*-nitrophenylsemicarbazide. In this respect, 1-*o*-nitrophenylsemicarbazide resembles urea. A mixture of urea and aniline, heated at 160°, gives rise to phenylurea and carbanilide, and under this condition urea serves as an excellent source of *iso*cyanic acid (Davis *et al*, *J. Amer. Chem. Soc.*, 1922, **44**, 2595; 1923, **45**, 1816; 1929, **51**, 1790, 1801, 1806).

The facility with which the decomposition of 1-*o*-nitrophenylsemicarbazide takes place is further demonstrated by its behaviour towards hot normal alkali, when benzoazimidol (Nietzki and Braunschweig, *Ber.*, 1894, **27**, 3381) is readily formed.

When, however, 1-phenylsemicarbazide is heated with aniline at 150-155°, 1 : 4-diphenylsemicarbazide is obtained and no trace of carbanilide is formed. This shows that 1-phenylsemicarbazide is much more stable than 1-*o*-nitro-phenylsemicarbazide.

EXPERIMENTAL

Action of Aniline upon 1-o-*Nitrophenylsemicarbazide : Isolation of Carbanilide.*
1-*o*-Nitrophenylsemicarbazide (3 g.; prepared according to the method of Guha and Ghosh, *loc. cit.*) was mixed with excess of aniline in a flask (aniline acts as a solvent also) and the mixture was heated in an oil-bath at 140-150° for 3-4 hours. The mass was then treated with excess of cold dilute hydrochloric acid and shaken vigorously when a solid came out which was filtered and washed several times with dilute hydrochloric acid and water. It crystallised from alcohol in colourless needles, m.p. 240-241°, yield 1 g. (Found : N, 13·48. $C_{13}H_{12}ON_2$ requires N, 13·20 per cent).

The identity of this compound with a genuine sample of carbanilide was confirmed by mixed m.p.

Action of p-*Toluidine upon* 1-o-*Nitrophenylsemicarbazide : Isolation of Sym-di-p-tolylurea.*—The method of procedure was the same as in the case of the previous reaction. The product was crystallised from alcohol, m.p. 266-268°, yield 1·2 g. from 3 g. of 1-*o*-nitrophenylsemicarbazide. (Found : N, 11·48. $C_{15}H_{16}ON_2$ requires N, 11·66 per cent). The identity of this compound with a genuine sample of sym-di-*p*-tolylurea was confirmed by mixed m.p.

Action of Alkali upon 1-o-*Nitrophenylsemicarbazide : Formation of Benzo-azimidol*
—1-*o*-Nitrophenylsemicarbazide (2 g.) was mixed with excess of normal aqueous caustic

potash solution and the mixture heated on the water-bath for about 1 hour. The brown solution was cooled and acidified with dilute hydrochlorid acid, when a brown solid was precipitated, which crystallised from hot water in colourless needles, m.p. 159-160°, yield 0·5 g. It gives a blood-red colouration with ferric chloride and is readily soluble in alkali. (Found : N, 31·31. $C_6H_5ON_3$ requires N, 31·11 per cent). Nietzki and Braunschweig (*loc. cit.*) recorded 157° as the m.p. of the compound.

Action of Aniline upon 1-Phenylsemicarbazide : Formation of 1 : 4-Diphenylsemicarbazide.—1-Phenylsemicarbazide (3 g.) was mixed with excess of aniline and the mixture was heated in an oil-bath at 150-155° for 3—4 hours, when ammonia was found to evolve. The mass was next treated with excess of cold dilute hydrochloric acid and shaken vigorously, when a solid was obtained, which was crystallised several times from alcohol in colourless needles, m.p, 170-172° (*cf.* Skinner and Ruhemann, *J. Chem. Soc.,* 1888, 53, 552). (Found : N, 18·32. $C_{13}H_{13}ON_3$ requires N, 18·50 per cent).

No trace of carbanilide was found in any of the above alcoholic extracts during crystallisation.

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DIELECTRIC CONSTANTS. OF INORGANIC SALTS

By N. V. Sathe, N. L. Phalnikar and B. V. Bhide

Dielectric constants of several inorganic and metallic salts of organic acids have been determined and also their refractive indices. Correlation of the dielectric polarisation and molecular refraction to deformability of ions has been attempted.

A study of the dielectric constant (D.C.) of inorganic salts (non-metallic ionic solids) reveals many interesting points. The D.C. of non-metallic ionic solids arises from 'the shift of the charge as in non-polar molecular solids, but the shift of ionic charge which contributes to P_i plays a more important part than the electronic effect.

The D.C. of the non-metallic ionic solids shows the following characteristics:—(i) The Maxwell's relation ($\epsilon \approx n^2$) does not hold good. (ii) Total polarisation and P_c in ionic solids increases with increase in the size of ions. (iii) Solids having a close packing have high D.C. (Frank, *Trans. Faraday Soc.*, 1937, **35**, 513). (iv) A polymorphic substance has the highest D.C. in its densest form [*e.g.*, Rutile (Density, 1.21; D.C., 114); Frank (*loc. cit.*]. (v) The D.C. varies along the different axes of the crystal. (vi) Most of the solids (with a few exceptions) have D.C. less than 10.

Another characteristic property of the ionic salts is that their properties can be expressed in terms of the properties of the ions. In other words, the properties are additive. However, many cases have been recorded where deviation from the rule of additivity has been observed. Refraction of salts can be given as an example of this.

The colour of some halides also supports the above statement. Divalent lead ion and the iodide ion are both colourless but when both the ions combine a coloured lead salt is obtained. The colour of at least one of the ions must have changed under the influence of the other. Thus the proximity of one ion to the other creates a deformation in the other ion. The deformation of ions thus influences many other properties of the salts. Among such properties, the refractive index (molecular refraction) has been studied to a great extent by Fajans and Joos (*Z. Physik*, 1924, **23**, 1; Fajans, *Z. physikal. Chem.*, 1927, **130**, 724) and Fajans (*Z. Elektrochem.*, 1928, **34**, 502) has developed a theory known as the theory of deformation.

Fajans (*loc. cit.*) has correlated the departure of the molecular refraction from the additivity rule with the size of ions. The interionic distances in the inorganic salts do not obey the rule of additivity owing to the deformation of ions. Moreover, Fajans from a study of the properties and their departure from the additivity rule has been able to correlate these properties with the type of the valence bonds. It is not, however, possible to find the refractive index of many solids ; hence to find a measure of the deformation, some other property of the solid must be studied. We thought that the determination of D.C. and polarisation may well serve as a measure of the deformation of the ions and also it may be interesting to see how the D.C. and polarisation are affected by the type of different linkages in the salts.

In the present work we have determined the D C. of inorganic salts and metallic salts of organic acids with a view to correlating dielectric polarisation and molecular refraction to the deformability of the ions.

E X P E R I M E N T A L

Purification of Salts.—All the salts used were of A.R. quality and were purified by crystallisation and obtained in the anhydrous form by fusion, if the salt did not decompose.

Solvents.—Xylene was dried over sodium and distilled. Nitrobenzene was fractionally distilled under reduced pressure.

Measurement of D.C.

Apparatus.—The apparatus used was the same as described by Bhide and Bhide (*J. Univ. Bom.*, 1938, **8**, Part III, 93) and Gokhale, Phalnikar and Bhave (*ibid.*, 1943, **11**, Part V, 56).

Method of measuring D.C.—The D.C. of salts in the powder condition was measured by the mixture method. The mixture method was first introduced by Starke (*Wied. Ann.*, 1897, **69**, 629) and Spater (*Ann. Physik*, 1902, **9**, 919), and was further improved by Höjendahl (*Z. physikal. Chem.*, 1933, **B 20**, 54).

In this method the D.C. of the mixture of two pure liquids of various compositions were found at various temperatures. The liquids used must be such that the salts were insoluble in them. The D.C. of the mixture was determined systematically by varying the proportion of the mixture till the D.C. of the solid and the mixture was the same. This was known when the condenser had the same capacity with the liquid mixture in and also after introducing the powder in the liquid mixture.

Another way was to find a temperature—D.C. curve for the liquid mixture and on introducing the powder to find the curve of D.C. and temperature. The point of intersection of these two curves gives the value of the D.C. Care is taken to see that the powder is uniform and the condenser is dipped in the powder and air pockets excluded. This was achieved by keeping the solid in contact with the liquid for some time and shaking and applying a slight vacuum to remove the occluded air.

Measurement of Refractive Index

Molecular refractions of some solids were found out by measuring the refractive indices of their solutions using a Bausch and Lomb dipping refractometer and calculating the molar refractions by Hedestrand's formula (*Z. physikal. Chem.*, 1929, **B 2**, 428).

From Table I the following deductions can be made :—

(*i*) Densities of salts studied increase from the chloride to bromide and from bromide to iodide of an element. Iodides of lead, silver and cadmium (β) are exceptions to this rule, as they have densities lower than the corresponding bromides.

(*ii*) The dielectric constants of salts also follow the above order, *viz.*, Cl < Br < I. Potassium chloride and potassium bromide have the same dielectric constant.

(*iii*) The molecular polarisation of iodide is greater than that of the bromide and of the bromide greater than that of the chloride of a metal. It will be noted that there is no exception to this generalisation. This is quite in accordance with the theory of deformation of Fajans. The size of ions increases from Cl to Br and Br to I. Therefore, the deformability increases. The polarisation depends on the deformability of the ion. This gives an explanation of the increase in dielectric polarisation from Cl to Br and from Br to I of a metal.

(iv)   The polarisations of potassium and silver salts (Table II) are nearly the same. This will be referred to later.

(v)   The density and dielectric constant of the polymorphic forms of HgI_2 and CdI_2 have also been given in the table.   The polymorphic forms have different densities and dielectric constants and also different molecular polarisations. HgI_2 (yellow) has a higher polarisation (64·31) than the red variety (58·97) and CdI_2 (β) has a higher polarisation (70·08) than the α-form (56·66).

TABLE I

Dielectric constant

Substance.	Density.	Present work.	Previous values	Molecular polarisation.	Molecular refraction
NaCl	2 161	6·29	6 29[3] 5·6[1] 6 28[9] 5 8[18] 6 12[5] 5·81[1] 9 3[2] 5·83[15]	17·26	8·52
NaBr	3·203	6·45	6·1[11]	20 72	13·17
NaI	3 655	7·17	6·15[11]	34·74	19·74
KCl ·	1 985	5·00	4·85[9] 4 79[9] 4·54[13] 3·97[12] 4·51[17] 2·42[10] 4·75[4] 5·03[5] 2·4[5] 4·94[3] 4·8[15] 4·64[16]	21·46	10·85
KBr	2 749	4·94	4·7[9] 4·6[11] 4 6[7]	24·58	13·98
KI	3·12	7 00	5·2[11] 5·6[9] 5·2[7] 5·17[18]	35·57	20·73
AgCl	5·501	14·13	10·9[9] 11·2[7]	21·21	13·43
AgBr	6 245	15·09	12·1[9] 12·2[7]	24·79	16·70
AgI	5 644	33 86	...	37·92	23·25
BaCl₂	3 913	8·42	11 44[9]	37·9	22 3
BaBr₂	4·575	8 66	12[9]	46·5	28·7
CaCl₂	2·150	5 85	...	31·9	18·75
CaBr₂	3·35ɔ	6·15	...	37 71	25·75
MgCl₂	2·320	4·42	...	21 87	17·69
MgBr₂	3·720	4 96	..	28·17	24 69
PbCl₂	5·912	39 06	42[9] 33·5[12] 25·06[17] 6·03[10] 4·6[5] 4·2[6] 6[5]	43 61	26·63

TABLE I (contd.)

Substance.	Density.	Present work.	Previous values.	Molecular polarisation.	Molecular refraction.
$PbBr_2$	6·648	42.6	42[9], 4 9[8]	51·50	33·62
PbI_2	6 078	113	113[9] 24[8]	74·53	47 94
$HgCl_2$	5·435	8·17	2·95[10] 3·2[8]	35 22	22·45
$HgBr_2$	6 035	9·84	...	44 60	29·45
HgI_2 (red)	7·070	34·32	...	58·97	42·05
(yellow)	6 282	25	...	64·31	...
$CdCl_2$	4·047	6·73	...	39·73	10·29
$CdBr_2$	5·192	7·32	...	34·24	13·93
CdI_2 (α)	5·670	22·5	...	56·66	20·3
„ (β)	4 660	25·6	...	70·08	...
$FeCl_2$	2·481	5·8	...	31·45	...
Na-acetate	1·518	4·44	...	28·83	14 52
K-acetate	1·815	5·56	...	32·61	16 85
Ag „	3·260	6·25	.	32·58	...
Ba „	2 424	5·44	..	48·35	24·82
Ca „	1·509	4·66	...	36·08	..
Pb „	3·12	7·79	...	59·17	35·41
Hg „	3·270	4·82	...	54·61	...
Cd „	2 194	5·11	...	60·72	...
Zn „	1·745	4·52	...	56·72	...
K_3 Fe (CN)$_6$	1 822	6·24	...	114·91	...
K_4 Fe (CN)$_6$	1·886	14·4	...	160 66	...

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16 J. Errera and H. Brasseur, Physikal. Z., 1933, 34, 369.

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18. Burton and Turnbull, Proc. Roy. Soc., 1937, 158, A, 182.

A few more interesting facts can be observed from the molecular polarisations of these salts. Table III gives the difference between the polarisations of a bromide and a chloride and that of an iodide and a bromide of an element.

TABLE II

Substance.	Chloride.	Bromide.	Iodide.	Acetate.
Potassium	21.45	24 57	35.57	32.61
Silver	21.21	24 79	37 92	32 58

TABLE III

Differences in dielectric polarisation between iodides and bromides and bromides and chlorides of salts.

Element.	MBr-MCl.	Diff. from the mean 3.4.	MI-MBr.	Element.	½(MBr₂-MCl₂).	Diff from the mean 3.4	½(MI₂-MBr₂).
Lithium*	3.67	0.27	4.01	Magnesium	3.15	−0.25	—
Sodium	3.46	0.06	14.0	Calcium	2.9	−0.5	—
Potassium	3.14	−0.26	10.89	Barium	4 3	0.9	—
Silver	3.58	0.18	13.1	Cadmium	2.3	−1.1	(a) form 11.2
				Mercury	4.5	1.1	yellow form 9.85
				Lead	3.9	0.5	11.5

* Steulmann, *Z. Physik*, 1932, **77**, 114 and Schupp, *Z. Physik*, 1932, **76**, 83.

TABLE IV

Element.	M(C₂H₃O₂)-MCl.
Sodium	11.57
Potassium	11.17
Silver	11 37
Barium	5.39
Mercury	9 7
Calcium	2 09
Cadmium	15.5
Lead	7.78

TABLE V

Element	Chloride.	Bromide.	Iodide.
Sodium	2.02	1.57	1.76
Potassium	1.98	1.76	1.62
Silver	1.59	1.49	1.63
Magnesium	1.24	1.14	—
Calcium	1.7	1.45	—
Barium	1.7	1 62	—
Cadmium	2.89	2 46	2.79
Mercury	1.57	1.51	1.53
Lead	1.64	1 53	1.55

It will be observed that the differences between the polarisations of the bromide and chloride (MBr—MCl) are nearly 3.4 which is the mean of the differences of all the salts given in the above table with the exception of barium, cadmium and mercury. As will be shown later that in the case of mercury and cadmium and to a certain extent in the case of lead this irregularity is to be expected. The rest of the salts therefore show that there is an additive relationship in the dielectric polarisation of the bromides and chlorides. The difference in the polarisation of the corresponding iodides and bromides do not show this regularity to any marked extent. This additive relationship is therefore not observed with iodides. This may be due to greater deformation possible in the case of the iodine ion (Fajans, *J. Chem. Phys.*, 1941, **9**, 282). The case of barium appears to be an exception.

The additive relationship is also seen in the case of alkali acetates and chlorides of metals. The differences in the polarisations of acetates and chlorides of metals are given in Table IV.

It will be seen that in the case of monovalent salts, *i.e.*, in the case of sodium, potassium and silver, the differences are surprisingly the same while in the case of bivalent salts examined, no such relationship is observed.

In Table V the ratios of the dielectric polarisations to molecular refractions of salts are given.

It will be observed that the ratio is always less in the case of bromide than in the chloride with the exception of K. This ratio is of the order : Cl > Br < I.

From the above observations it will be seen that salts which have a definite ionic structure show certain regularity in their physical properties such as density, dielectric constants, dielectric polarisations, etc., while AgI, PbI₂ HgI₂ and CdI₂ show considerable departure from these regularities.

The structures of these salts will now be discussed in the light of experimental and theoretical data other than dielectric polarisation.

These salts are coloured ; moreover PbI₂, MgI₂ and CdI₂ have layer lattice while AgI shows an ionic lattice. The atomic distances in these salts are considerably less than those required for ionic substances.

The diamagnetism of $CdBr_2$, CdI_2, and ZnI_2 have been examined by Subramaniam (*Proc. Ind. Acad. Sci.*, 1936, **4A**, 404). He finds that there is a considerable increase in magnetic susceptibilities of these salts in solution. Ionic solids like KCl do not show this behaviour. The increase in susceptibility in solution is attributed to the change in the linkage due to the interaction of the solvent. CdI_2 and ZnI_2 are suppposed to be partially co-valent in the solid condition and on solution they are split up into ions due to a loosening of the bond by the action of the solvent. In the case of $HgCl_2$ there is no such change on solution. This is regarded as an exception.

Tables VI and VII give the lattice energies and the observed and calculated ionic distances in the case of silver halides.

<table>
<tr><td colspan="4" align="center">TABLE VI</td><td colspan="5" align="center">TABLE VII</td></tr>
<tr><td colspan="4" align="center">*Lattice energy.**</td><td colspan="5" align="center">*Ionic distances.*</td></tr>
<tr><td>Salts.</td><td>Obs.</td><td>Calc.</td><td>Difference.</td><td>Salt.</td><td>Ionic.</td><td>Co-valent</td><td>Obs.</td><td>Difference.</td></tr>
<tr><td>AgCl</td><td>213 9</td><td>203</td><td>11 9</td><td>AgCl</td><td>3 07</td><td>2 52</td><td>2 77</td><td>0 30</td></tr>
<tr><td>AgBr</td><td>210·9</td><td>197</td><td>13·9</td><td>AgBr</td><td>3 21</td><td>2 64</td><td>2·88</td><td>0·33</td></tr>
<tr><td>AgI</td><td>208·2</td><td>190</td><td>18 2</td><td>AgI</td><td>3·42</td><td>2 81</td><td>2·99</td><td></td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td>3·28</td><td>2·81</td><td>2·80</td><td>0·48</td></tr>
</table>

It will be seen that the deviation from the observed anion-cation distances and the calculated ionic distance becomes progressively more pronounced as we pass from chloride to bromide and iodide. Likewise the difference between experimental and theoretical lattice energies become progressively greater. Moreover, AgCl and AgBr have NaCl type of lattice whereas AgI has a tetrahedral type of lattice, which is recognised as a characteristic of co-valent linkage. This type of lattice is of course to be expected with ionic linkage if the ratio of cation : anion radii is small enough ; but the ratio is not

* Mayer, *J. Chem. Phys.*, 1933, 1, 327, .270 ; Mayer and Levy, *ibid.*, 1933, 1, 647.

small in the case of AgI. In addition it is believed that the increasing insolubility of Ag salts is directly connected with an increasing co-valent character. The size of the Ag ion is only slightly smaller than that of K. This explains the close parallelism between the polarisation of Ag and K salts (Table II).

To summarise, the evidence of AgI being regarded as partly co-valent is (i) crystal form (tetrahedral), (ii) increase in difference between observed and calculated lattice energies, (iii) increase in difference between observed and calculated ionic distances. The only point in favour of regarding AgI as ionic is its electrical conductivity in the solid condition. Therefore we may conclude that the linkage between Ag and I is of the transition type, i.e., between electro-valent and co-valent.

The following tables (VIII and IX) give the lattice energies observed and calculated, and ionic distance of PbI_2 and CdI_2 respectively.

TABLE VIII

*Lattice energy.**

Salt.	Obs.	Calc.	Difference
PbI_2	497·1	457·7	39·4
CdI_2	563·1	473·6	89·5

TABLE IX

Ionic distances.

Salt	Obs.	Ionic.	Covalent.
$CdCl_2$	2·66	2·59	2·47
CdI_2	2·99	2·95	2·76

The crystal form of CdI_2 is a remarkable mixture of molecular, non-polar and ionic forces, the crystal consisting of layers. Each layer consists of three planes—one of Cd atom surrounded on either side by a plane of equal number of iodine ions. The molecules are thus held together mostly by Van der Waal's forces. This is quite unlike ionic crystals.

Table X gives the observed internuclear distances for Hg salts.

TABLE X

Ionic distances.

Salt.	Obs.	Ionic.	Co-valent.
$HgCl_2$	2·25	2 43	2·47
$HgBr_2$	2·48	2·56	2·12
HgI_2	2·78	2 98	2·76

TABLE XI

Salt.		Dielectric constant.	Dielectric polarisation.
AgI		33·86	37·92
HgI_2	(red)	34·32	58·97
HgI_2	(yellow)	25	64 31
PbI_2		113	74·53
CdI_2	(α)	22·5	56·66
CdI_2	(β)	25·6	70·08

In the case of HgI_2 the observed distance (2·78) is very close to the distance required for a co-valent linkage (2·76) while that for the ionic linking amounts to 2·98.

From the above it will be seen that HgI_2, AgI, PbI_2 and CdI_2 have definitely an intermediate type of linkage. The salts show abnormally high dielectric constants en

* The values of lattice energies for CdI_2 and PbI_2 are taken from the calculations of Sherman (Chem. Rev., 1932, 11, 93). These values are not very accurate but the difference in the calculated and observed values of lattice energies is sufficiently large and from what has been said about AgI it will be clear that CdI_2 and PbI_2 are predominently co-valent (Fitzer and Hildebrand, J Amer. Chem. Soc, 1941, 63, 2472). They have discussed the relationship of colour and bond character and are of opinion that AgI and CdI_2 are partially ionic.

high dielectric polarisation. Ionic salts possess generally a dielectric constant varying between 5 and 10. Table XI illustrates this point.

The dielectric constant of ferrous chloride is 5·8, nearly of the same order as shown by the ionic type of crystals. Therefore $FeCl_2$ belong definitely to the compounds of the electro-valent type. It was intended to find the dielectric constant of ferric chloride, which is known to have a co-valent linkage. But the compound is soluble in organic solvents used and hence its dielectric constant could not be determined.

The dielectric constants of potassium ferricyanide and potassium ferrocyanide were determined with a view to finding out the effect of complex ions on the dielectric constants of the salts. The dielectric constants of these salts are : $K_3Fe(CN)_6$, 6·24 ; $K_4Fe(CN)_6$, 14·4.

The dielectric constants are comparatively low and thus these salts resemble other ionic salts. Errera and Brasseur (*Phys. Z.*, 1933, **34**, 369) have determined the dielectric constants of calcium, strontium, magnesium and barium platinocyanides. The dielectric constants of these salts range from 5 to 9 showing that these salts also belong to the ionic type.

The molecular refractions of acetates in acetic acid could be determined only for those of sodium, potassium, barium and lead as these were the only acetates soluble in acetic acid. The data, however, are incomplete for a detailed comparison. The ratios of the dielectric polarisation to molecular refractions of these acetates are given below.

<p align="center">TABLE XII</p>

Salt.	Dielectric polarisation.	Molecular refraction.	Ratio.
Na-acetate	28 83	14·516	1·986
K-acetate	32·61	16·830	1·936
Ba-acetate	48 35.	24·816	1·930
Pb-acetate	59·18	35·409	1·672

It will be seen that in the case of sodium, potassium and barium acetates the ratio is nearly 2, which is also found in the case of the corresponding ratio of sodium and potassium chlorides. The interpretation of these results on other lines is being carried out by one of us (N. V. S.) with Dr. S. K. K. Jatkar and will be published in another paper.

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PHENYLTHIOCARBAMIDES. A CONTRIBUTION TO THE STUDY OF THE TRIAD -N-C-S. PART XVI. THE SUPPOSED FORMATION OF DISULPHIDES BY THE OXIDATION OF THIOCARBAMIDES

By Ramchandra Sahasrabudhey and Hans Krall

Evidence is adduced to controvert the general belief that unstable disulphides of the formamidine type are the first products of oxidation.

It has been suggested from time to time (for references *vide* this journal, 1944, **21**, 17) that in the oxidation of thiocarbamides to thiodiazoles, disulphides are formed as unstable intermediate products but we are not aware of any direct experimental evidence in support of this supposition.

We have already shown (*loc. cit.*) that, contrary to the observation of Dost, a methylphenylthiocarbamide forms an aminobenzthiazole derivative by the action of sulphur monochloride in chloroform, and not a disulphide or a hydrazodithiodicarbonamide.

This agrees with the observations of Hofmann and Gabriel (*Ber.*, 1892, **25**, 1578) and of De and Chakravarty (*J. Indian Chem. Soc.*, 1928, **5**, 661) who oxidised the same thiocarbamide with iodine or hydrogen peroxide and obtained a thiazole, but does not agree with Lal and Krall (*ibid.*, 1937, **14**, 478) who claimed to have obtained methylphenylformamidine disulphide by the action of nitrous acid.

We have therefore re-examined their picrate, finding it to be the picrate of Hofmann and Gabriel's thiodiazole, and we have also isolated the thiodiazole itself. We find no indication of disulphide formation.

We have also oxidised phenylthiocarbamide with nitrous acid in a strong acid medium in the presence of picric acid, when any disulphide formed, even as an intermediate product, should be picked up by the picric acid, but the picrate of Hector's base alone was obtained. This confirms the view of Lal and Krall (*ibid.*, 1939, **16**, 31) that Hector's base is a primary product, and is not produced *via* a disulphide.

Fromm (*Annalen*, 1915, **394**, 284) working with compounds which were expected to give dithio-formamidines came to the similar conclusion that Hugershoff's diazothiol (*Ber.*, 1903, **36**, 3130) is formed from s-diphenylthiocarbamide directly and not through a disulphide.

Lal and Krall (*J. Indian Chem. Soc.*, 1938, **15**, 217) obtained no disulphide by the action of nitrous acid on s-methylphenylthiocarbamide. but, under all conditions directly obtained a base probably a thiodiazole $C_{16}H_{14}N_4S$ (they give $C_{16}H_{15}N_4S$).

Vidya Sagar and Krall (*ibid.*, 1940, **17**, 475) studied the closely related thiobenzamide but found no evidence of disulphide formation under any conditions.

We conclude, therefore, that aryl thiocarbamides do not yield disulphides on oxidation.

EXPERIMENTAL

Expt. 1.—Oxidation of a-methylphenylthiocarbamide with nitrous acid in 1 : 1 ratio of the reactants in a normal hydrochloric acid medium.—Methylphenylthiocarbamide (8·3 g., 1/20th mole) was dissolved in 200 c.c. of 50% alcohol. 100 C.c. of 4N-hydrochloric acid were added to this. An aqueous solution of sodium nitrite containing 3·5 g.

(1/10th mole) in 100 c.c. of water was then gradually run into the thiocarbamide solution during the course of ½ hour. The mixture was constantly stirred. During the earlier stages of the reaction a red colouration developed which eventually faded away. The mixture was allowed to stand for about 1 hour to complete the reaction. A little amorphous yellow solid matter separated out which was filtered and the filtrate examined as follows :—

(i) A part of the clear filtrate was treated with an excess of aqueous picric acid. A crystalline yellow precipitate separated out which on crystallisation from methyl alcohol melted ot 142-43°.

(ii) A portion ot the filtrate was made alkaline with ammonia and extracted with ether. The ethereal extract on evaporation left (a) crystals of sulphur, (b) colourless crystals of m.p. 93-94°, (c) a viscous brown liquid which on standing for over a week deposited crystalline plates of the unreacted thiocarbamide. The crystalline compound of the m.p. 93-94° gave a yellow picrate (m.p. 142°) with picric acid, its identity with the picrate obtained in (i) above was established by a mixed m.p.

Expt. 2.—Hofmann and Gabriel's thiodiazole was prepared by Chakravarty's method using hydrogen peroxide as the oxidising agent, m.p. 94-95°. It also gave a picrate of m.p. 142° identical with the picrate described in Expt. 1. Further it was found that on treatment with excess of alkali thiodiazole could be recovered from the picrate of Exp. 1 (i).

Expt. 3.—Oxidation of phenylthiocarbamide with nitrous acid in presence of picric acid.—Phenylthiocarbamide (1·5 g.) was dissolved in about 100 c.c. of warm aqueous picric acid solution containing about 5 c.c. of concentrated hydrochloric acid. Sodium nitrite (0·7 g.) dissolved in a little water was gradually added. A voluminous yellow precipitate was immediately formed. No other product could be isolated. Crystals from dilute alcohol melt at 203° (mixed m.p. with the picrate from Hector's base).

QUINOLINE DERIVATIVES. PART IX

By T. N. Ghosh and A C. Roy

For pharmacological study against amoebiasis, some quinoline derivatives, in which both 8-ethoxy-quinoline residue and the fundamental nucleus of Carbarsone or Stovarsol are present, have been prepared.

As a result of extensive clinical trials of various chemotherapeutic drugs on cases of amoebic dysentery in the army, Leishman and Kelsall (*Lancet*, 1944, p. 231) have found that there are some relapsing cases which resist the action of all these drugs. They have felt the urgent need for the discovery of a new amoebicidal drug, which will effect cure in chronic and relapsing cases.

Derivatives of 8-hydroxyquinoline, such as Chinosol, Yatren and Vioform, are widely used in cases of amoebic dysentery. Again organo-arsenical compounds, such as Carbarsone and Stovarsol (3-acetylamino-4-hydroxyphenylarsonic acid), are also used as useful amoebicidal drugs. It was thought of interest to prepare compounds in which both 8-hydroxyquinoline or its derivative and the fundamental nucleus of Carbarsone or Stovarsol are present, and to find out if such compounds possess amoebicidal properties.

As on direct sulphonation, and so with chlorosulphonic acid, 8-hydroxyquinoline yields 8-hydroxyquinoline-5-sulphonic acid, the iodo derivative of which constitutes the drug, Yatren. However, 8-ethoxyquinoline yields, with chlorosulphonic acid, 8-ethoxy-quinoline-5-sulphonyl chloride which has been condensed with *p*-arsanilic acid and with 3-amino-4-hydroxyphenylarsonic acid to give respectively the compounds (I) and (II), the pharmocological examination of which is under investigation.

$$SO_2R$$

$$OEt \quad N$$
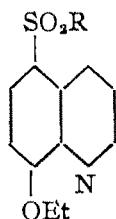
[(I), R = $-NH-C_6H_4-AsO(OH)_2$ (1 : 4).   (II), R = $-NH-C_6H_3(OH)-AsO(OH)_2$ (3 : 4 : 1]

EXPERIMENTAL

8-Ethoxyquinoline was prepared according to the method of Fischer and Renouf (*Ber.*, 1884, **17**, 759), b.p. 285-86°, straw-coloured, heavy liquid, yield 55 g. from 60 g. of 8-hydroxyquinoline.

8-Ethoxyquinoline-5-sulphonyl Chloride.—In a round-bottomed flask, fitted with a mechanical stirrer, were placed 75 g. of chlorosulphonic acid, previously distilled from a glass retort. The flask was cooled to about 12°. To the chlorosulphonic acid was added gradually 17 g. of 8-ethoxyquinoline, temperature being maintained between 12° and 15°. After the addition was over, the mixture was heated at 65°-70° in an oil-bath for about 3 hours. The syrupy liquid was cooled in ice and poured slowly, with stirring, into excess of melting ice. A brown, clear solution was obtained which was immediately saturated with sodium chloride. The clear thick solution, on scratching and standing for about

30 minutes, deposited a voluminous precipitate, which was filtered, pressed on the Buchner and dried quickly on a porous plate, yield 16 g. The crude sulphonyl chloride was used for subsequent operations without purification. On standing for a day, the mother-liquor gradually deposited a crystalline solid which proved to be 8-ethoxy-quinoline-5-sulphonic acid. It was crystallised from hot water in light brown, shining needles, m.p. 286-88° (decomp.), yield 3 g. It is readily soluble in aqueous sodium bicarbonate. (Found: N, 5·46. $C_{11}H_{11}O_4NS$ requires N, 5·53 per cent).

8-*Ethoxyquinoline-5-sulphonamidophenyl-4'-arsonic Acid* (I).—To a solution of *para*-arsanilic acid (12 g.) in a solution of sodium carbonate (6 g. in 150 c.c. of water) 8-ethoxy-quinoline-5-sulphonyl chloride (14 g.) was gradually added with stirring. With efferve-scense a pasty mass was precipitated, which, on vigorous stirring with a glass rod, became granular solid powder. The solution at this stage was found very faintly alkaline. Anhydrous sodium carbonate (3 g.) and water (100 c.c.) were further added and the mixture was stirred with a glass rod for 3-4 hours, when an almost clear solution was obtained. Next day, the solution was filtered and the clear filtrate was just acidified with pure concentrated hydrochloric acid (just acid to litmus), when a heavy precipitate was obtained, which was filtered and washed with water. It is sparingly soluble in boiling water and was boiled with large quantity of water to remove any *para*-arsanilic acid. The residual solid was twice crystallised from alcohol as a colourless, crystalline powder, m.p. 242-44° (decomp.), yield 6 g. It is readily soluble in cold dilute hydrochloric acid and also in cold dilute aqueous sodium bicarbonate. (Found: N, 5·93; As, 17·01. $C_{17}H_{17}O_6N_2S$ As requires N, 6·19; As, 16·57 per cent).

8-*Ethoxyquinoline -5- sulphonamido -2'- hydroxyphenyl-5'-arsonic Acid* (II).—The method of preparation was the same as in the case of the previous compound. 3-Amino-4-hydroxyphenylarsonic acid (12 g.), 8-ethoxyquinoline-5-sulphonyl chloride (crude, 14 g.) and anhydrous sodium carbonate (9 g.) were used. The reaction mixture was filtered and acidified with glacial acetic acid. On standing and scratching for some time, a precipitate was obtained which was filtered and washed with water. It is sparingly soluble in boiling water and was boiled 2-3 times with sufficient quantity of water and filtered. It is insoluble in hot alcohol and glacial acetic acid. For purification, it was dissolved in the requisite quantity of aqueous sodium carbonate and the solution, after being mixed with norit, was stirred for sometime. After filtration, the solution was acidified with acetic acid, when a colourless granular solid was obtained. It was filtered, washed with water and alcohol, and dried in the air. It was finally dried in *vacuo* at 120°, m.p. 215-17° (decomp.), yield 5·5 g. (Found: N, 5·72; As, 15·29. $C_{17}H_{17}O_7N_2SAs$ requires N, 5·98; As, 16·00 per cent). It is readily soluble in cold dilute hydrochloric acid and in cold aqueous sodium bicarbonate solution.

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ACRIDINE DERIVATIVES. PART I

By M. L. Aggarwal, I. Sen-Gupta and B. Ahmad

Some 5-substituted 3-amino-6-chloro-acridnes have been synthesised for studying their antiseptic properties

In view of the fact that diaminoacridines possess bactericidal properties (Albert, Francis, Garrod and Linnell, *Brit. J. Exp. Path.*, 1938, **19**, 41), it was thought interesting to synthesise acridines with an anilino or halogenated anilino group in position 5 of the general formula (V).

HOOC

O_2N

NO_2

Cl

NH
(I)

Cl
5
4
3
2
1
6
7
8
9
N
(II)

Cl Cl
O_2N
N
(III)

NHR Cl
O_2N
N
(IV)

NHR Cl
H_2N
N
(V)
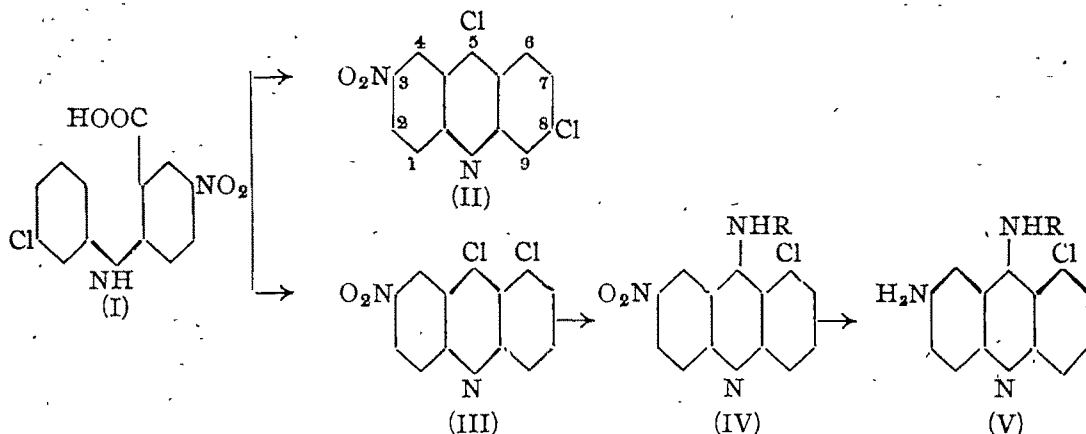
For this purpose *m*-chloroaniline has been condensed with 2-chloro-5-nitrobenzoic acid, and 4-nitro-3'-chlorodiphenylamine-6-carboxylic acid (I), thus formed, is cyclised with phosphorus oxychloride to give two isomeric 5:8-dichloro-3-nitro- and 5:6-dichloro-3-nitro-acridines (II and III) out of which only (III) was isolated. To confirm the position of chlorine in the above acridine, an alternative synthesis of 5:8-dichloro-3-nitroacridine (II) has been carried out by condensing *p*-nitroaniline with 2:4-dichlorobenzoic acid to give 4'-nitro-3-chlorodiphenylamine-6-carboxylic acid which is subsequently cyclised with phosphorus oxychloride. Bradbury and Linnell (*J. Chem. Soc.*, 1942, 377) also prepared 4-nitro-3'-chlorodiphenylamine-6-carboxylic acid in 23% yield by a very tedious method but under our conditions a yield of 60% is obtainable. The yield of the acridine (III) has also been largely improved.

5:6-Dichloro-3-nitroacridine has been further condensed with aniline, *p*-anisidine, *p*-chloroaniline, *m*-chloroaniline, *p*-bromoaniline, *o*-bromoaniline, *o*-iodoaniline and 2:3-di-chloroaniline. Two of these nitro acridines have been successfully reduced using fused stannous chloride and hydrochloric acid. Reduction with the reagent described by Linnell (*J. Chem. Soc.*, 1936, 1617) did not yield satisfactory results. The bactericidal properties (against streptococci) of these nitro-and aminoacridines are under investigation.

EXPERIMENTAL

4-Nitro-3'-chlorodiphenylamine-6-carboxylic Acid.—*m*-Chloraniline (2·5 g., 2 mols) was heated with 2·5 g. of 2-chloro-5-nitrobenzoic acid at 150-160° for 12 hours. The reaction product was rubbed with dilute hydrochloric acid, filtered and washed well with acetone, when a yellow coloured compound was left. It was crystallised from glacial

acetic acid in bright yellow needles (1·9 g.), m.p. 276°. (Bradbury and Linnell give m.p. 272-73°). (Found : N, 9·74. Calc. for $C_{13}H_6O_4N_2Cl$: N, 9·57 per cent).

4'-Nitro-3-chlorodiphenylamine-6-carboxylic Acid.—2 : 4-Dichlorobenzoic acid (1·9 g., .1 mol.), *p*-nitroaniline (2 g. 1·5 mol.), anhydrous. potassium carbonate (2 g.) and 0·1 g. of copper-bronze were powdered and moistened with amyl alcohol (5 c.c.). The whole thing was heated at 140° for 12 hours and amyl alcohol removed by distillation and finally by passing steam. The residue was boiled with additional amount (2 g.) of potassium carbonate and filtered hot. The insoluble potassium salt left on the filter paper was acidified with hot dilute hydrochloric acid and the greenish insoluble mass crystallised from toluene in light yellow flakes (0·48 g.), m.p. 235°. (Found : N, 9·61. $C_{13}H_9O_4N_2$ Cl requires N, 9·57 per cent). The yield could not be improved, though several attempts using nitrobenzene, glycerol, etc. were made.

5 : 6-Dichloro-3-nitroacridine.— 4- Nitro-3'- chlorodiphenylamine -6- carboxylic   acid (4 g.) was heated with phosphorus oxychloride (24 c.c.) at 145-150° for 10 hours. After cooling the excess of phosphorus oxychloride was removed by petroleum ether and the residue treated with 10% ice-cold aqueous ammonia, filtered and left overnight. Next day it was stirred with 20 c.c. of cold acetone, dried and crystallised from benzene when it came out as light yellow flocculant crystals (1 g.), m.p. 201°-202°. (Found :. N, 9·64. $C_{13}H_6O_3N_2Cl_2$ requires N, 9·55 per cent).

5 : 8-Dichloro-3- nitroacridine.—4'- Nitro -3- chlorodiphenylamine -6- carboxylic   acid (1 g.) was heated with 6 c.c. of phosphorus oxychloride at 110-115° for 45 minutes and at 145° for 10 minutes. The reaction was worked up as above except that after treatment with ice-cold ammonia, it was not left overnight but worked up at once. The acridine of slight greenish yellow colour came out of benzene (2 g.), m.p. 227° (Bradbury and Linnell recorded m.p. 223° for the same isolated from the mixture). (Found : N, 9·75. Calc. for $C_{13}H_6O_3N_2Cl_2$: N, 9·55 per cent).

3-Nitro-6-chloro-5-(p-anisidino)   acridine.—5 : 6-Dichloro 3-nitroacridine   (0·5 g.) was heated with *p*-anisidine (0·21 g., 1 mol.) along with phenol (1 g.) at 110-120° for 2 hours. The reaction mixture was triturated with dry ether and filtered when the hydrochloride of the condensation product was obtained in quantitative yield. It was basified with ammonia and crystallised from alcohol in brown powdery crystals, m.p. 264°. (Found : N, 10·86. $C_{20}H_{14}O_3N_3Cl$ requires N, 11·08 per cent). ·

3-Nitro-6-chloro-5-(p-chloroanilino) acridine.—The acridine (0·5 g.), heated with molecular quantity (0·21 g.) of *p*-chloroaniline under the above conditions and working up as above, gave the corresponding acridine as yellowish red crystal, m.p. 216-17°. (Found : N, 10·76. $C_{19}H_{13}O_2N_3Cl_2$ requires N, 10·03 per cent).

3-Nitro -6- chloro-5 (2 : 5- dichloroanilino) acridine.—2 : 5- Dichloroaniline, when condensed with the same acridine under the above conditions, gave quantitative yield of the hydrochloride of the condensation product which came out as orange flakes after basifying with ammonia and crystallising from alcohol, m.p. 253-55°. (Found : N, 9·88. $C_{19}H_{10}O_2N_3Cl_3$ requires N, 10·03 per cent).

3-Nitro-6-chloro-5 (o-iodoanilino) acridine.—o-Iodoaniline, condensed with the acridine under the same conditions, yielded reddish crystals of the corresponding acridine, m.p. 225-26°. (Found : N, 9·17. $C_{19}H_{11}O_2N_3ClI$ requires N 9·17 per cent).

3-Nitro-6-chloro-5 (*p-bromoanilino*)*acridine.*—The reaction between bromoaniline (0·31 g.) and dichloronitroacridine (III) proceeded better in toluene (refluxing for 6 hours) than phenol. The reaction was worked up by filtering and washing with ether basifying and crystallising from alcohol, m.p. 214-15°. (Found : N, 9·54. $C_{19}H_{11}O_2N_3ClBr$ requires N, 9·8 per cent).

3-Nitro-6-chloro-5 (*o-bromoanilino*) *acridine.*—The acridine (0·5 g.) was directly heated with *o*-bromoaniline (0·3 g., 1 mol.) at 110-120° for 2 hours. The reaction product was worked up by triturating with ether, basifying and crystallising from alcohol and a base, m.p. 245°, was obtained. (Found : N, 10·05. $C_{19}H_{11}O_2N_3Cl$ Br requires N, 9·8 per cent).

3-Nitro-6-chloro-5 (*m-chloroanilino*) *acridine.*—The acridine (0·5 g.) was directly heated with molecular amount of *m*-chloroaniline (0·21 g.) at 110-120° for 2 hours. The reaction mixture worked up as above yielded bright red crystals of a base, m.p. 106-107° (decomp.). (Found : N, 10·88. $C_{19}H_{11}O_2N_3Cl_2$ requires N, 10·94 per cent).

3-Nitro-6-chloro-5 (*anilino*) *acridine.*—Aniline when heated with the acridine in molecular proportion under the same conditions yielded the corresponding acridine, m.p. 270°. (Found : N, 12·26. $C_{19}H_{13}O_2N_3Cl$ requires N, 12·0 per cent).

3 - Amino - 6 - chloro - 5(*p-bromoanilino*)*acridine.*—3-Nitro-6-chloro-5(*p*-bromoanilino)-acridine (0·5 g.) was suspended in 1·5 c.c. of concentrated hydrochloric acid and 1·5 g. of stannous chloride (powdered) were slowly added with continuous trituration and the whole thing heated on a sand-bath. The tin double salt was collected by suction, dissolved in water (15 c.c.), filtered and basified with a concentrated solution of potassium hydroxide. The base was collected, washed free from alkali, dried and crystallised from benzene in light yellow flakes, m.p. 234-35° (0·2 g.) with previous shrinkage at 229°. (Found : N, 10·16. $C_{19}H_{13}N_3Cl$ Br requires N, 10·52 per cent).

3-Amino-6-chloro-5 (*m-chloroanilino*) *acridine.*—3-Nitro-6-chloro-5(*m*-chloroanilino)-acridine (0·5 g.) on reduction as above yielded brownish yellowish flakes of the corresponding amino compound, m.p. 212° with previous shrinkage at 208°. (Found : N, 11·44. $C_{19}H_{13}N_3Cl_2$ requires N, 11·8 per cent).

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COMPOSITION OF PRUSSIAN AND TURNBULL'S BLUES. PART VII. VISCOSITY IN RELATION TO COMPOSITION

By Wahid U. Malik and Abani K. Bhattacharya

The viscosity of the colloidal Prussian and Turnbull's blues has been determined at various stages of dialysis and dilution and at several temperatures. It has been observed by plotting the values of viscosity against (i) the days of dialysis, and (ii) against dilution, that at the same temperatures the viscosity curves are remarkably similiar in shape showing that the composition of the colloidal Prussian and Turnbull's blues also tend to become identical. Changes in viscosity with temperature lead to the same conclusion.

The view that the electric charge on the suspensoid particles contribute to the viscosity of the system containing such particles was first put forward by Smoluchowski (*Trans. Faraday Soc.*, 1913, **9**, 35). This view was further supported by Ostwald and Hatschek in their study on the viscosities of various hydrosols.

Dhar and Gore (*J. Indian Chem. Soc.*, 1929, **6**, 641) carried out investigations on the changes of viscosity of many colloids and observed that the lesser the charge on the colloids, the greater was its hydration and hence greater was the viscosity. They observed a definite relation between viscosity and purity of various hydroxide sols, but could not establish any definite relation in the case of arsenic and antimony sulphide sols as well as copper ferrocyanide and Prussian blue sols. The reason for the irregular behaviour was supposed to be due to their gradual hydrolysis with the progress of dialysis.

In this paper, we have discussed the results of our investigations on the behaviour of Prussian and Turnbull's blue sols from the view point of their viscosity at various stages of dialysis and temperature. From the viscosity of these sols we have attempted to throw some light on the similarity of their composition as well.

EXPERIMENTAL

Preparation of the Sols.—In order to bring Prussian blue in the colloidal state excess of potassium ferrocyanide was used and it was found that, on mixing one equivalent of ferric chloride with 5/4 equivalents of potassium ferrocyanide, a fairly stable sol was obtained. A more stable sol was prepared by mixing the reactants in the ratio of one equivalent to 1·5 equivalents.

Turnbull's blue was brought into the colloidal state by using excess of potassium ferricyanide solution. It was found that on mixing one equivalent of ferrous sulphate with 1·5 equivalents of potassium ferricyanide a fairly stable sol was obtained.

Measurement of Viscosity.—Scarpa's method (*Gazzetta*, 1910, **40**, 271) modified by Farrow (*J. Chem. Soc.*, 1912, **101**, 347) and improved by Prasad, Mehta and Desai (*J. Phys. Chem.*, 1932, **36**, 1384) was followed. An ordinary viscometer was kept in an electrically heated thermostat and a suction at a pressure of 15 cm. of water was applied throughout our investigations in order to cause the upward flow of liquid into the viscometer. The apparatus constant K was determined at several temperatures by the formula :

$$\eta_{t^0} = K\frac{t_1 t_2}{t_1 + t_2},$$

where η_{t^0} = the absolute viscosity of water at t^0,

t_1 = time required by the liquid to rise from the lower to the upper mark,

t_2 = time required by the liquid to fall from the upper to the lower mark.

The values of K at different temperatures are given below :

Temp. ...	21°	25°	27 5°	30°	32·5°	35°
K ...	0·001336	0·001211	0·001202	0·001171	0·001140	0·001117

The apparatus was standardised before it was used for measurement of the viscosity of the sols. The concentration of the sol on each day of dialysis was kept constant and the viscosity of the original sol 'A' and those of twice and four times diluted ones ("A/2" and "A/4") were also observed.

FIG. 1

Change of viscosity with dialysis
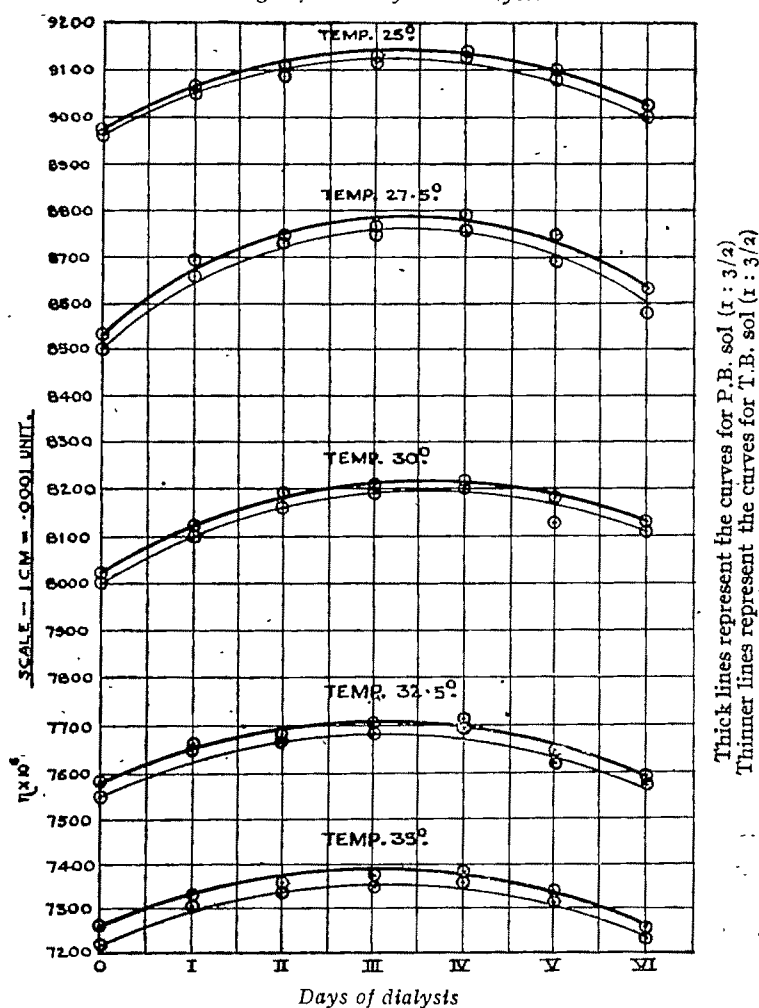
Thick lines represent the curves for P.B. sol (1 : 3/2)
Thinner lines represent the curves for T.B. sol (1 : 3/2)

Days of dialysis

Results have been presented in graphs. Fig. 1 gives the variations in viscosity with the progress of dialysis for Prussian blue and Turnbull's blue prepared with iron salt : potassium salt in the ratio (1 : 1·5). Fig. 2 shows the same results for Prussian blue prepared in the ratio of iron to potassium salts as 1 : 1·25.

3—1547P—2

Variations of viscosity with dilution at different stages of dialysis for both Prussian blue and Turnbull's blue sols prepared with iron salt : potassium salt in the ratio of 1 : 3/2 have been graphically shown in Fig. 3.

DISCUSSION

From the foregoing results it will be observed that the viscosity of both these sols gradually rises as the purity increases for the first four days, after which there is a fall. Fig. 1 shows this effect very clearly.

Dhar and collaborators observed that no definite relation regarding the viscosity and the purity of the sol could be established in the case of hydrolysable sols, such as Prussian blue, arsenic and antimony sulphide sols. Our investigations, however, show that Prussian and Turnbull's blue sols behave upto a certain stage of dialysis in the same way as unhydrolysable sols which exhibit increase in viscosity as their purity increases by dialysis. The viscosity values in the curves clearly show that there is a regular increase in the viscosity of the Prussian and Turnbull's blue sols for the first four days of dialysis, and then on further dialysis, the viscosity begins to decrease. A scrutiny of the curves will show, that the maximum increase in viscosity takes place on the first day of dialysis and then the rate of increase becomes less and less till the fourth day, when the viscosity reaches maximum. On the fifth and sixth days there is a decrease. This can be explained by assuming that there are two different states of the colloid during the course of its dialysis. The first state of the sol corresponds with the view advocated by Dhar and Gore (loc. cit.) that the viscosity increases with the hydration of colloidal particle caused by the dialysis of the sol, and the second state is one where the progressive hydration stops and then the hydrolysis of the sol follows.

It is further observed that the viscosity maximum (Fig. 2) reaches on the second day

FIG. 2

Changes in viscosity with dialysis of P B. sol (1 : 5/4).
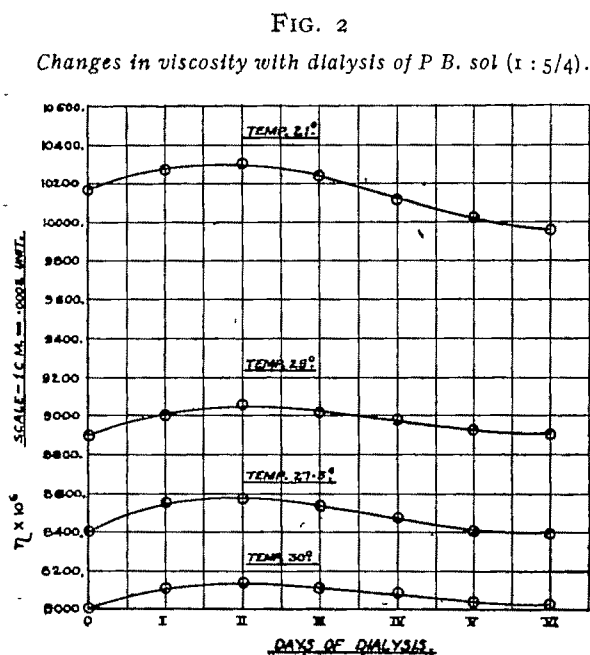
of dialysis in the case of the sol's prepared by mixing the reactants in the ratio of one equivalent to 5/4 equivalents, whereas the viscosity maximum of the sol prepared by mixing one equivalent of ferric chloride with 3/2 equivalents of potassium ferrocyanide reaches on the fourth day. Turnbull's blue sol prepared by mixing the reactants in the ratio of one equivalent to 5/4 equivalents was not very stable while that prepared by mixing the reactants in the ratio of one equivalent to 3/2 equivalents shows a similar maximum on the fourth day of dialysis. This observation suggests that the similarity of behaviour of these two sols is much influenced by the amount of potassium ferro- and ferricyanide added in excess during their preparation.

FIG. 3
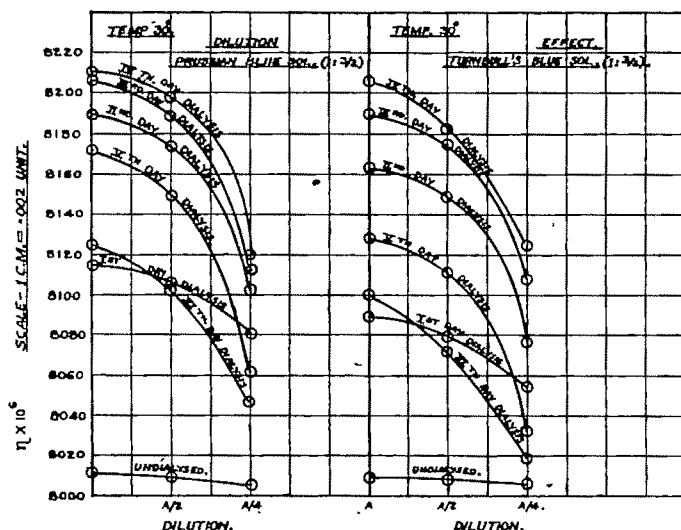
Their behaviour on dilution at different stages of dialysis (Fig. 3) shows that the changes in viscosity with dilution are such as to yield curves of similar shape.

The relation between the changes in viscosity with temperature shown by Prussian and Turnbull's blue sols seems to be almost linear and the straight lines thus obtained for the respective sols begin to overlap each other after the third day of dialysis.

Bhattacharya and Dhar (Z. anorg. Chem., 1933, **213**, 248) advanced the view that precipitated Prussian and Turnbull's blues should have similar composition. This view was supported by analytical results as well as by physical properties such as absorption

FIG. 4

Relation between temperature and viscosity
for P.B. sol (1 : 3/2)
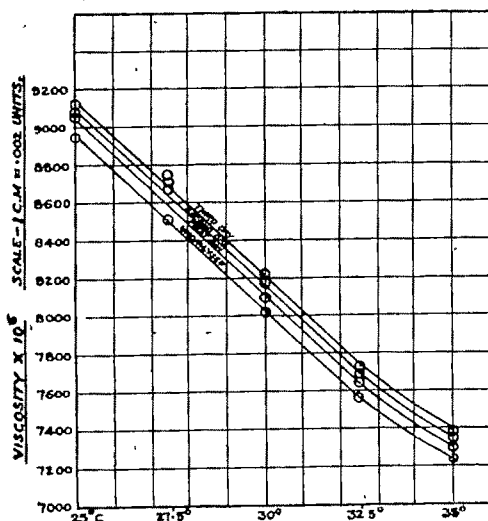
FIG. 5

Relation between temperature and viscosity
for T.B. sol (1 : 3/2).
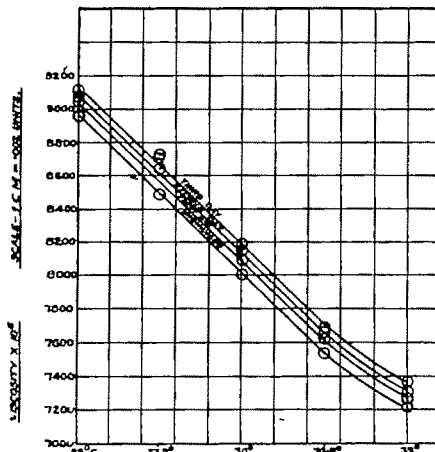
spectra and magnetic susceptibility of such compounds as were prepared by the ageing method (Bhattacharya, *J. Indian Chem. Soc.*, 1934, **11**, 325; 1935, **12**, 143; 1941, **18**, 71). By studying the viscosities of the sols of Prussian and Turnbull's blues, we conclude that the composition of the colloidal solutions prepared by mixing one equivalent to 3/2 equivalents also tend to approach each other very closely as has been observed in the case of the precipitates of aged Prussian and Turnbull's blues by Bhattacharya. The little shift between the closely approaching curves having identical shapes as in Fig. 1, only suggests that there is some difference in the size of the colloidal particles of Prussian and Turnbull's blues while the chemical composition of these two colloidal substances as judged from these curves seems to be the same. The mutual oxidation and reduction between the reactants is much greater when potassium ferrocyanide or ferricyanide is added in excess to ferric chloride and ferrous sulphate respectively than when the reactants are mixed in equivalent proportion. It is due to this effect followed by the adsorption of ferro- or ferricyanogen ions that the composition of the sols of Prussian and Turnbull's blues shows such a marked similarity as can be judged from the changes of their viscosities with dialysis.

THE MOLECULAR COMPOUNDS OF 4:6-DIBROMO-1:3-DINITROBENZENE*

By C. N. Adaveeshiah and H. Subba Jois

Molecular compounds of 4 6-dibromo-1·3-dinitrobenzene with α-and β-naphthols, α-and β-naphthyl-amines, naphthalene, acenaphthene, phenanthrene, pyridine and urotropine have been isolated. W·th naphthylamines, pyridine and urotropine condensation products have also been isolated.

Sudborough and Picton (*J. Chem. Soc.*, 1906, **89**, 589) and later Jois and Manjunath (*J. Indian Chem. Soc.*, 1931, **8**, 633) prepared molecular compounds of 4:6-dichloro-1:3-dinitrobenzene with α- and β-naphthylamines. In addition, the latter have isolated molecular compounds with naphthalene, α- and β-naphthols, benzidine and pyridine. In the present investigation molecular compounds of 4:6-dibromo-1:3-dinitrobenzene have been prepared with a view to studying how the introduction of two bromine atoms into *m*-dinitrobenzene influences the formation and stability of molecular compounds.

4:6-Dibromo-1:3-dinitrobenzene forms molecular compounds with α-and β-naphthols, α-and β-naphthylamines, naphthalene and pyridine. In addition, molecular compounds with acenaphthene, phenanthrene and urotropine have been isolated. All the molecular compounds except those of pyridine and urotropine possess deep colour. The molecular ratio is 1:1 except with pyridine and urotropine. Two molecules of pyridine unite with one molecule of the nitro compound to form a dipyridonium salt (*cf.* Jois and Manjunath, *J. Mysore Univ.*, 1932, **6**, 13) of the following structure:—
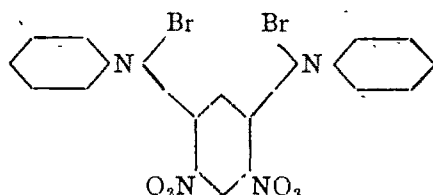
The molecular compound with urotropine, on the other hand, contains two molecular proportions of the nitro compound with one of urotropine. Dimethylaniline, diphenylamine and quinoline give only red solutions but molecular compounds could not be isolated. Anthracene, fluorene, diphenyl, *p*-toluidine, benzidine, *o*-, *m*- and *p*-nitroanilines do not give any indication of the formation of molecular compounds. With benzidine condensation takes place readily and molecular compound could not be isolated in a pure state. As Buehler (*J. Amer. Chem. Soc.*, 1930, **52**, 1941) puts it, molecular compounds are probably intermediates in the formation of condensation products.

The molecular compounds of 4:6-dichloro-1:3-dinitrobenzene appear to be more stable and more easily formed than the corresponding compounds with 4:6-dibromo-1:3-dinitrobenzene. Similar observation is made by Buehler (*loc. cit.*) with molecular compounds of 2:4-dinitrochlorobenzene and the corresponding bromo derivative.

4:6-Dibromo-1:3-dinitrobenzene, required for this investigation, is prepared starting with acetanilide which is converted into *m*-dibromobenzene by modifying the method of Jackson and Cohoe (*Amer. Chem. J.*, 1901, **26**, 3). *m*-Dibromobenzene is then nitrated to yield mostly 4:6-dibromo-1:3-dinitrobenzene according to the method of Nietzki and Shelder as modified by Jois and Manjunath (*J. Mysore Univ.*, 1930, **4**, 239).

ÉXPERIMENTAL

The molecular compounds except these of pyridine and urotropine were prepared by dissolving the two components in molecular proportions separately in a suitable solvent and mixing the hot solutions. On cooling, crystals separated and were recrystallised from the same solvent. The molecular compound with pyridine was prepared and purified in the same manner as was adopted by Jois and Manjunath (*loc. cit.*) in the preparation of the molecular compound of pyridine and 4:6-dichloro-1:3-dinitrobenzene. To prepare the molecular compound with urotropine the two components in the proper proportion were dissolved in dry acetone, mixed and set aside for some days, when a mixture of the condensation product and the molecular compound separated. From this mixture a pure sample of the molecular compound was obtained by dissolving in methyl alcohol and precipitating with ether. The other details regarding the molecular compounds are given in Table I.

Condensation Products

Condensation Product of (A) *with a- Naphthylamine : 2:4- Dinitro-5-bromophenyl-a-naphthylamine.*—When the molecular compound (3) was dissolved in alcohol and refluxed for about 1/2 hour, the condensation product gradually separated. This is found to exist in two modifications, yellow and red. The former was obtained by crystallising the crude condensation product from benzene, xylene or ethyl acetate and the latter by refluxing the benzene solution and allowing it to cool. The yellow form was also obtained directly by refluxing the components in molecular ratio in alcoholic solution, m.p. 191-92°, red variety, m.p. 191-92° and its melting point was not lowered when mixed with the yellow form. [Found (yellow form): Br, 20·5; (red form): Br, 20·8. $C_{16}H_{10}O_4N_3$Br requires Br, 20·6 per cent).

Condensation product of (A) *with β-Naphthylamine: 2:4-Dinitro-5-bromophenyl-β-naphthylamine.*—This was formed readily on heating a solution of the molecular compound (4) in alcohol and was found to exist in two forms, orange and red. The former was obtained by crystallising the crude condensation product from ethyl alcohol, methyl alcohol or better from acetone and the latter from benzene. The red variety changes over to the orange variety slowly on keeping, rapidly on heating to 110-115°. Both the varieties melt at 192·93° and the melting point is not lowered by mixing the two. [Found (orange form): Br, 20·6, (yellow form): Br 20·8. $C_{16}H_{10}O_4N_3$Br requires Br, 20·6 per cent]. The orange or red variety gives intense red colour with concentrated sulphuric acid, while the corresponding condensation product of a-naphthylamine develops an intense bluish green colour.

Condensation product· of (A) *with Pyridine.*—The molecular compound (3) on heating either alone or with water changes over to the condensation product with elimination of hydrogen bromide. It is best prepared by heating pyridine (2 mols.) with 4:6-dibromo-1:3-dinitrobenzene (1 mol.) for some time on the water-bath and then boiling with water for a few hours. It is crystallised from boiling water as golden yellow needles. It does not melt but decomposes with explosive violence at about 340°. (Found: N, 17·6. $C_{16}H_{10}O_4N_4$ requires N, 17·4 per cent).

Condensation product of (A) *with Urotropine.*—The yellow residue that separated from the molecular compound (6) was washed repeatedly with hot methyl alcohol and then crystallised from boiling acetone in which it is sparingly soluble, when yellow crystals were obtained. It is very sparingly soluble in water and in the ordinary organic solvents, and melts with decomposition at 201-202°. (Found: N, 17·6; Br, 25·5. $C_{18}H_{14}O_8N_6Br_2$ requires N, 17·8; Br, 25·4 per cent).

TABLE I

Molecular Compounds of 4:6-dibromo 1:3-dinitrobenzene (A) *with* (B)

No.	B	Molecular ratio A:B	Solvent used.	Form of the compound.	M.p.	Molecular formula.	Analysis	
							Calc.	Found.
1	α-Naphthol	1·1	CCl₄	Yellow prismatic crystals.	91-92°	$C_{16}H_{10}O_5N_2Br_2$	Br 34·0	Br, 34·1
2	β-Naphthol	1:1	Do	Orange-yellow prismatic crystals.	83-84°	$C_{16}H_{10}O_5N_2Br_2$	Br, 34·0	Br, 34·3
3	α-Naphthyl-amine.	1·1	Do.	Dark-red prismatic crystals.	80-80·5°	$C_{16}H_{11}O_4N_3Br_2$	Br, 34·1	Br, 34·3
*4	β-Naphthyl-amine.	1·1	Ligroin	Chocolate-red prismatic needles.	61·5-62·5°	$C_{16}H_{11}O_4N_3Br_2$	Br, 34·1	Br, 34·4
**5	Pyridine	1:2	(same method as described by Jois and Manjunath, *loc. cit*).	Colourless micro-crystalline.		$C_{16}H_{12}O_4N_4Br_2,$ $2H_2O$	N, 10·8 Br, 30·8	N, 10·5 Br, 30·8
†6	Urotropine	2:1	Acetone	Colourless needles.	...	$C_{18}H_{16}O_8N_8Br_4,$ $4H_2O$	Br, 37·0	Br, 37·0
††7	Naph-thalene	1:1	Absolute alcohol	Lemon-yellow crystals	66·67°	$C_{16}H_{10}O_4N_2Br_2$	Br, 35·2	Br, 35·5
‡8	Phenan-threne.	1:1	Do	Yellow needles.	66·5°	$C_{20}H_{12}O_4N_2Br_2$	Br, 31·7	Br, 31·5
‡‡9	Acenaph-thene	1·1	Do.	Deep-yellow needles	58-60°	$C_{18}H_{12}O_4N_2Br_2$	Br, 33·3	Br, 33·6

* Ether or CCl₄ gives only condensation product The molecular compound changes to the condensation product on keeping even at the room temperature

** The compound is soluble in alcohol and water but insoluble in ether and benzene. It ionises in aqueous solution and gives precipitate with silver nitrate solution On heating it gradually changes to the yellow compound decomposing at 165°.

† Soluble in water, ionises in aq. soln. and gives a precipitate with silver nitrate On heating the compound changes to a yellow product m.p. with decomp. at 201-202°.

†† The compound is not stable in the hot.

‡ The compound turns orange on keeping for some days.

‡‡ On exposure, colour deepens to brown.

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PARACHOR AND RING STRUCTURE. PART I

By W. V. BHAGWAT

The structural value for the parachor of a ring containing n-members is not independent of the nature of the members constituting the ring and hence is not the same even when n is the same. When two rings are superimposed the parachor decreases.

Sugden ("Parachor and Valency," p. 39) believes that the value calculated for six membered ring from the consideration of benzene ring holds for all rings of six, whether they may be of benzene type or not. It was suggested from our laboratories [Thesis submitted for M.Sc., 1942, 1944 by Moghe and Desai (unpublished) to Agra University] that the view needs modification. Mumford and Phillips (*J. Chem. Soc.*, 1928, 155; 1929, 2112; *Ber.*, 1930, **63**, 1818) were the first who objected to Sugden's procedure. Gibling *J. Chem. Soc.*, 1941, 300, 304) holds similar view. In this part of the paper, Sugden's values for ring structures have been considered. The recent work of Pauling (*Chem. Rev.*, 1921, **5**, 185; *J. Amer. Chem. Soc.*, 1931, **53**, 1367, 3225; 1932, **54**, 988, 3570; *J. Chem. Phys.*, 1933, **1**, 362, 606, 679) on resonance has changed our ideas of fixed structures of organic compounds which may resonate between various possible forms and hence produce net effect due to all, yet the determination of structure by parachor has its own value.

Bhatnagar and Singh (*J. chim. phys.*, 1928, **26**, 21) have calculated the parachor of naphthalene ring to be equal to 9.3. Sugden suggested that the value of naphthalene ring might be best represented if it is supposed to be composed of two separate six membered rings. Assuming this value 12.2 they determined the parachor of several compounds of naphthalene. The parachor of acenaphthalene was determined by Dutoit and Friedrich (*Arch. Sci. Phys. Nat.*, 1900, **9**, 105). The following table shows that the value 12.2 gives better results than the value 9.3. However, the naphthalene ring structure is not exactly twice of that of benzene as one side with double bond is common and as such it is expected that the value should be less than twice that of benzene ring or less than 12.2. The value should be calculated by the usual method, *i.e.*, by subtracting the calculated value without naphthalene ring from the observed values. This has been done in the present investigation and the results are recorded below.

TABLE I

Substance.	P (obs.).	P (calc.) with 12.2.	P (calc.) with 9.3.	P (calc.) without ring.	Difference of value of the ring.
Naphthalene	312.5	313.0	310	300.8	11.7
Acenaphthalene	364.2	365.3	362.4	353.1	11.1
α-Bromonaphthalene	362.6	363.9	361.0	351.7	10.9
α-Naphthol	326.5	326.3	323.4	314.1	12.4
α-Naphthylamine	341.6	342.6	338.7	330.4	11.2
β-Naphthylamine	341.6	342.6	338.7	330.4	11.2

Mean ... 11.45 *i.e.* 11.5

The structural value 11·5 for naphthalene ring will reproduce values better than the value 12·2 and hence it is suggested as the correct value for the parachor of naphthalene ring. The value as expected is less than that of two benzene rings.

The value of the parachor of phenanthrene determined by Bhatnagar and Singh (*loc. cit.*) is 414·1, while the calculated value on the basis of three benzene rings is 418·9. Comparison of the structure of phenanthrene shows that it is less than three benzene rings as two sides are common and is also less than the sum of naphthalene and benzene ring as one side is common.
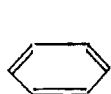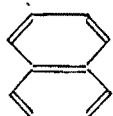
Benzene   Naphthalene   Phenanthrene
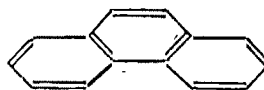
And hence its ring parachor is expected to be less than $3 \times 6 = 18$ and $11·5 + 6·1 = 17·6$. The value calculated for phenanthrene omitting the value of the ring is 400·6. This differs from the observed value 414·1 by 13·5. The ring value for phenanthrene is therefore 13·5, and is in accordance with our expectation that it should be less than 18 and also 17·6.

Paraldehyde is formed by the condensation of three molecules of acetaldehyde and its parachor is found by Schiff (*Annalen*, 1884, **223**, 47), Morgan and Stone, (*J. Amer. Chem. Soc.*, 1913, **35**, 1505) and Sugden (*J. Chem. Soc.*, 1924, **125**, 1177). This corresponds to cyclic formulae. The value calculated for cyclic formulae assuming the contribution of the ring as 6·1 is 300·1, while for open chain it is 317·2 and for $(CH_3 CHO)_3$ it is 363·6.
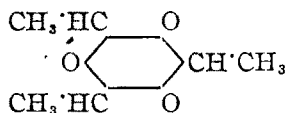
Here again the observed value is less by 1·4 units than the calculated value for ring structure. This is obvious because the ring is quite different from benzene ring. Not only does it contain the oxygen atoms in the ring but the double bonds are absent.

The work of Ray (*J. Indian Chem. Soc.*, 1934, **11**, 501) on five and six membered rings supports these views although Ray himself has failed to note the difference between pyridine ring and benzene ring.

TABLE II

Substance.	P (obs).	P (calc.) without ring.	P ring.
Pyridine	197·4	191·6	5·8
Piperidine	230·0	224·6	5·4
Picoline	236·3	230 6	5·7

It is therefore concluded that pyridine ring has a structural value 5·7. It is further to be noted that piperidine ring which contains no double bond has a value slightly differ-

4—1547P—2

ent from the other two. Ray's work (*loc. cit.*) on five membered ring compounds, pyrrole, and succinimide gives as low a value as 3·1 in place of the accepted value 8·5 while inden, phthalic anhydride and indole, which contain a ring of six in addition, gives much lower values than 14·6 which is obtained purely on additive basis. The fact that the observed value is lower than the sum of two rings again supports the view that when two rings are superimposed the value tends to decrease.

TABLE III

Substance.	P(obs.).	P (calc.) without ring	Difference (obs.)	Difference (theor.)
Inden	284·9	272·8	12·1	14·6
Phthalic anhydride	295 1	282·8	12·3	14·6
Indole	270·2	263·4	6·8	14·6

It is obvious therefore that the parachor is not a strictly additive function depending on the number of atoms in a ring, but also depends on the nature of the atoms constituting the ring.

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A NOTE ON THE SUPERSATURATION COEFFICIENT AND THE PARTICLE SIZE OF THE SOLUTE

By B. S. SRIKANTAN

Wollaston, (*Phil. Trans.*, 1813, **103**, 57) observed that finely divided solids not only dissolve more rapidly but also to a greater extent than relatively coarse particles. Gibbs (*Scientific Papers*, 1906, **1**, 315), J. J. Thomson ("Applications of Dynamics to Physics and Chemistry," 1888, 25) and Ostwald (*Z. physikal. Chem.*, 1900, **34**, 395) from different theoretical considerations have proposed an equation connecting solubility and the size of particles. Thus

$$\log_e S/S_1 = \frac{2M\sigma}{RT\,d}\{1/r - 1/r_1\}$$

where S and S_1 are the solubilities at radii r and r_1; T, the temperature (abs.); M, the molecular weight; d, the density; σ, the energy per unit area of the surface of separation between the solid and the liquid and R, the gas constant.

In the equation cited above, at any particular temperature and for the same substance, $\frac{2M\sigma}{RTd}$ is a constant (k). If r is infinitely great, then the solubility S_1 is the normal saturation solubility S_n. Then

$$\log_e S/S_n = k/r$$

If $k/r < 1$, S/S_n becomes equal to $(1 + kr)$ neglecting higher powers of k/r. The supersaturation coefficient defined by $(S - S_n)/S$ becomes equal to k/r. The expression $[r(S - S_n)]/S_n$ thus becomes constant.

This means that at constant temperature, the supersaturation coefficient of a (supersaturated) solution is inversely proportional to the size of the particle with which that solution is in equilibrium.

This is illustrated by an example from the solubility of gypsum taken from Mellor ("Comprehensive Treatise on Inorganic Chemistry" Vol. I, p. 508). Solubility data are expressed in milli moles per litre.

TABLE I

Size	Solubility at		
	0°	20°	35°
0·5 × 10⁻³ mm	14·4	16·5	17·0
1·0	13·5	15·8	16·3
3·0	13·1	15·3	15·75
5·0	12·85	15·0	15·5
From International Crit. Tables	12·92	15·1	15·5

TABLE II

Size	$(S - S_n)/S_n = K$		
0·5μ	0·057	0·050	0·049
1·0	0·052	0·053	0·052
3·0	0·057	0·060	0·048

Hence $5·0\mu$ can be taken to be r_∞ and the corresponding solubility as S_n.

Considering that the data have been taken from a graphical representation the constants are fairly good.

As a consequence of this law, it is obvious that the introduction of larger size particles would tend to diminish $(S - S_n)/S_n$ or the crystal will grow and converse is the case if a smaller particle than that in equilibium is introduced. This is in accordance with the experimental findings of Hulett (*J. Amer. Chem. Soc.*, 1902, **24**, 667).

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OBITUARY

JAGADINDRA NATH LAHIRI

Born : March 1, 1894.   Died :   December 22, 1944.

Jagadindra Nath Lahiri was the youngest son of the Late Pandit Durgadas Lahiri. He had his early education in his village school at Bantra, close to Calcutta, in the Howrah District. He passed I.Sc. and B.Sc. Examination from the St. Xavier's College. He obtained his M.Sc. degree in chemistry of the Calcutta University from the Presidency College in 1919 and had his research training under the guidance of Late Sir P. C. Ray in the Presidency College, Indian Association of Science and the University College of Science.

He joined the Bengal Chemical and Pharmaceutical Works as an Asst. Chemist on a salary of Rs. 75 per month in May 5, 1919. His keen sense of duty, perseverance and inordinate interest for the development of the company earned him gradually the position of the Chief Chemist, Factory Superintendent and ultimately the manager of the biggest chemical concern in India. His soft heartedness, unassuming disposition and amiable behaviour made him endeared to the meanest worker of the organisation. He was well known for his active habit and used to work 15-16 hours at a stretch. Lately he developed symptoms of high blood pressure which unfortunately caused his untimely death.
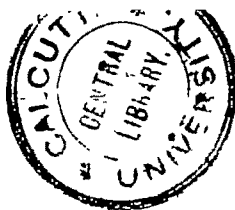
THE HYDROGEN-OXYGEN COMBINATION IN A SIEMEN'S OZONISER

By A. Jogarao

Gaseous mixtures of hydrogen and oxygen were subjected to the electric discharge in a Siemen's ozoniser. Gas pressures up to 50 cm. of Hg and applied potentials of 2000-4000 volts were employed. The current-potential relationship as well as the variation of the gas pressure with time were investigated for different values of applied potential, $H_2 : O_2$ ratio, and total initial gas pressure. The sudden and large changes in the secondary current looked for at the threshold potentials were only noticed in systems where the initial gas pressure was below 10 cm. of Hg.

The union of hydrogen and oxygen as well as the decomposition of water vapour when subjected to electric discharges has been extensively studied by several workers. Kirkby (*Phil. Mag.*, 1907, **13**, 299 ; 1905, **17**, 185 ; *Proc. Roy. Soc.*, 1911, **85**, A, 151) made a critical investigation of the hydrogen oxygen reaction in a discharge tube and correlated the amount of water formed with the gas pressure and the different electrical factors. Finch and others (*Proc. Roy. Soc.*, 1931, **133**, A, 173 ; 1930, **129**, A, 672 ; 1926, **111**, A, 257 ; 1927, **116**, A, 529) studied the cathodic combustion of hydrogen and oxygen mixtures at sputtering and non-sputtering cathodes. Löb (*Z. Elektrochem.*, 1906, **12**, 282 ; *Ber.*, 1908, **41**, 1517) reported the formation of hydrogen peroxide on subjecting moist carbon dioxide to silent electric discharge. Comanducci (*Gazzetta*, 1909, **40**, 600) investigated the effect of the silent electric discharge on various gaseous mixtures including that of hydrogen and oxygen. The reaction between the last two gases was studied in the electrodeless discharge by Rodebush and co-workers (*J. Phys. Chem.*, 1937, **41**, 283) and in the silent electric discharge by Fisher and Wolf (*Ber*, 1911, **44**, 2956 ; *Z. Elktrochem.*, 1914, **20**, 204). Chattock and Tyndall (*Phil. Mag.*, 1908, **14**, 24) studied the changes of pressure which accompany point-discharges through hydrogen containing oxygen and nitrogen. The reverse reaction namely the decomposition of water vapour was also studied by numerous workers (Keanbaum, *Compt. rend.*, 1910, **151**, 319 ; Linder, *Phys. Rev.*, 1931, **38**, 679 ; Urey and Lavin, *J. Amer. Chem. Soc.*, 1929, **51**, 3290 ; Rodebush and Wahl, *J. Chem. Phys.*, 1933, **1**, 696 ; Langmuir, *J. Amer. Chem. Soc.*, 1906, **28**, 1357) under conditions obtaining in different regions of a discharge tube and also in various other forms of electric discharge. The chemical effects of electrical discharges with special reference to ionisation and the reaction velocity have been dealt with at length by Poma (*Gazzetta*, 1921, **2**, 58), Briner (*J. chim. phys.*, 1915, **13**, 18 ; 1914, **12**, 526, 534), Lunt (*Nature*, 1936, **137**, 404 ; Elliot, Joshi and Lunt, *Trans. Faraday Soc.*, 1927, **23**, 57), Joshi and co-workers (*ibid.*, 1927, **23**, 227 ; 1929, **25**, 108, 118, 137) ; Joshi and Sharma (*J. chim. phys.*, 1934, **31**, 511) ; Finch and others (*Proc. Roy. Soc.*, 1931, **133**, A, 173 ; 1934, **143**, A, 482) ; Emeleus and Kennedy (*Phil. Mag.*, 1934, **18**, 874) ; Boulind (*Phil. Mag.*, 1934, **18**, 909) ; Max Le Blanc and Davies (*Z. Elektrochem.*, 1908, **14**, 361), Susumu Miyamoto (*J. Sci. Hiroshima Univ. Japan*, 1932, **2**, 218). Investigations on the passage of silent electric discharge through nitric oxide and through mixtures of hydrogen and chlorine which were conducted by Joshi and co-workers (not published) showed that gradual increases of the secondary voltage applied to the reaction mixture in the ozoniser caused

sudden and large change in the secondary current at the values of the threshold potentials. The work described below was undertaken with a view to examining the nature of variation of the secondary current and gas pressure with the applied potentials and the duration of the discharge in the case of hydrogen and oxygen mixtures.

EXPERIMENTAL

Fig. 1 is a diagrammatic representation of the general disposition of the apparatus employed which is essentially similar to the one used by Joshi and co-workers (*loc. cit.*). Circulation of water through the outer jacket tube **J** served to maintain the temperature of the reacting gaseous mixture contained in the annular space **RC** of the ozoniser constant during the passage of the electric discharge. The energy needed for maintaining

FIG. 1
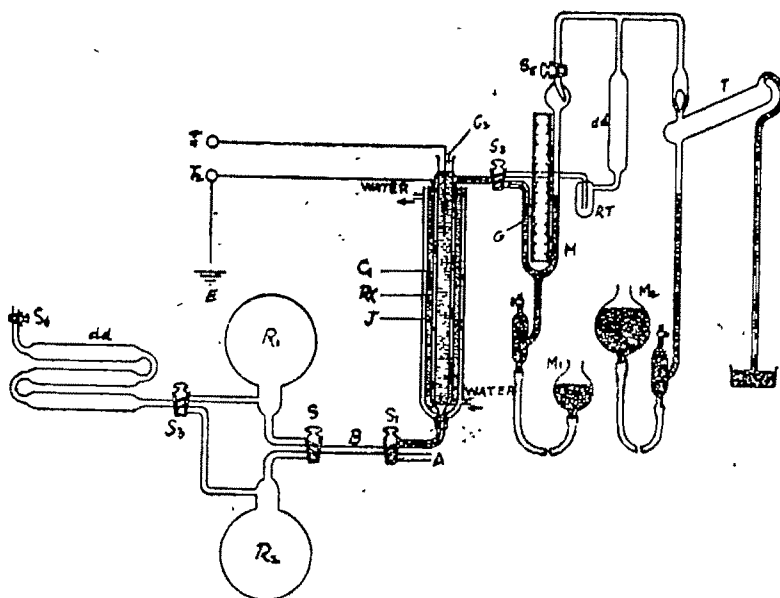
dd—Drying tubes packed with $CaCl_2$ or P_2O_5
R_1 & R_2—Gas reservoirs for H_2 & O_2
RC—Annular space of the ozoniser.
C_1 & C_2—Electrode chambers with conducting liquid
J—Jacket for cold water circulation.
M—Hg manometer
T—Töpler pump.
M_1 & M_2—Hg reservoirs.
T_1 & T_2—Secondaries of the transformer.
S_1 to S_6—Vacuum stop-cock.

the electric discharge was supplied by means of a rotary converter and an oil-immersed step-up transformer with a maximum range of 40,000 volts, connected through suitable resistances and a switch. The secondary terminals T_1 and T_2 of the transformer were connected to two strips of metal immersed in the electrolyte solution contained in the

electrode chambers C_2 and C_1 respectively. The terminal T_2 was also earthed. The current flowing through the reaction chamber could be measured by means of a sensitive microammeter placed in the earthing circuit. The actual potential applied could be varied at will by regulating the resistance in the primary circuit of the transformer and its exact value was computed from the reading of the voltmeter placed across the primary circuit and the transformer-ratio. This experimental arrangement enabled single phase alternating current at any potential to be applied to the reaction mixture and the corresponding gas pressure or secondary current to be read from time to time. The entire apparatus was made of glass and ground glass joints or rubber tubing for connecting the different pieces of the apparatus were avoided. Only good quality vacuum grease was used for the stop-cocks. After thorough exhaustion of the air in the apparatus by means of a Cenco Hyvac and the Töpler pumps, the resulting vacuum measured by means of a McLeod gauge was found to be of the order of 5×10^{-4} cm. of Hg, and this was considered sufficient for purposes of these studies.

The following are the dimensions of the reaction chamber used :—

Inner diameter of the inner tube	...	1·3 cm.
Outer diameter of the inner tube	...	1·5 ,,
Thickness of the wall	...	0·1 ,,
Inner diameter of the outer tube	...	1 8 ,,
Outer diameter of the outer tube	...	2 1 ,,
Thickness of the wall	...	0·15 ,,
Mean width of the annular space	...	0·15 ,,
Mean length of the annular space	...	27·45 ,,
Volume of the annular space excluding that of the connecting capillaries	...	22·4 c.c

Taking the usual precautions, the gas reservoirs R_1 and R_2 were first filled with pure dry hydrogen and oxygen respectively, to serve as stock for all the experiments. The required quantities of the two gases were then enclosed in the annular space RC of the ozoniser, so as to give a mixture having the desired $H_2 : O_2$ ratio and the total initial gas pressure. During the whole course of the experiment, and in particular when recording the reading of the manometer, care was taken to see that the mercury in the left limb was always maintained just touching the tip of the glass index G inside the limb. This was done by raising or lowering the mercury reservoir M_1. The difference in height between the mercury levels in the two limbs gave the pressure of the gaseous mixtures under investigation.

After switching on the current, the resistances in the primary circuit of the transformer were carefully regulated in order to maintain the secondary voltage at the desired value and the discharge was allowed to pass for the necessary length of time. The pressure reading of the manometer was recorded at regular intervals of time, and so too the micro-ammeter readings.

In those series of experiments, which were carried out with a view to examining the current-voltage relationship, the general procedure adopted as a rule was to start with a low applied potential and gradually increase it to about 4000 volts in a number of steps, recording at the same time the micro-ammeter reading at each step. Also before raising

the potential to a new value, the reaction mixture was maintained under the existing potential for a time-interval of about one to three minutes in order to enable any falling tendency of the gas pressure under the influence of the electric discharge, which was indicative of the progress of the chemical reaction, to be noted.

DISCUSSION

Curves I to XI shown in Fig. 2 give the variations of the gas pressure with time in a few typical experiments. The figures within brackets represent the total initial gas pressure, p, the hydrogen : oxygen ratio, r, the applied potential, V, respectively. In curve I the applied potential was 2,700 volts during the first 78 minutes, but it was

FIG. 2

Duration of discharge in min.
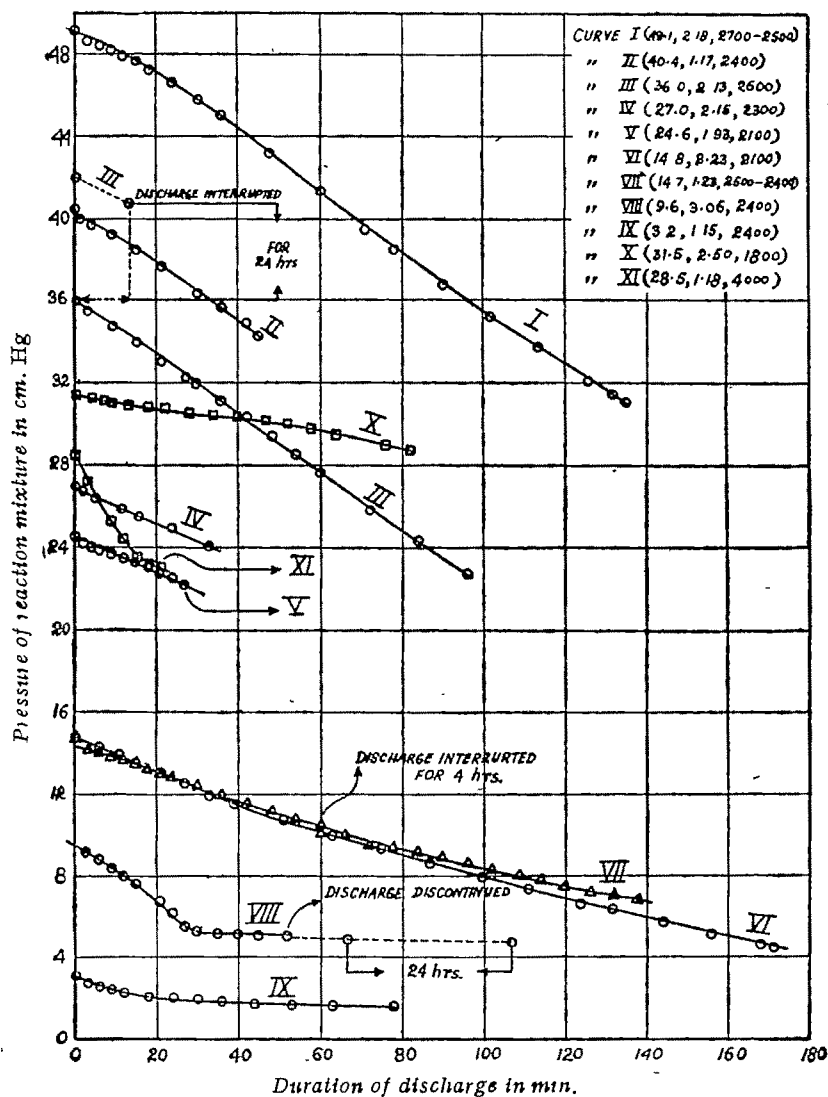
dimished to 2,500 volts for the remaining period. In curves, II, IV, V, VI, VIII, IX and X, the potential was gradually raised to the values indicated against them after a brief intermittant trial at lower voltages, and the time and manometer readings were started after the respective voltages were brought to their final values. In curve III, the actual initial gas pressure was 41·95 cm., but after a few brief trials lasting for nearly 13 minutes at voltages ranging up-to 2,600, the discharge was interrupted for 24 hours. At the end of the 24 hours' period of interruption the gas pressure fell down to 36 cm. This is indicated by the dotted portion of the curve III. The discharge was recommenced at 2,600 volts and continued for 96 minutes, and the corresponding pressure-time readings were plotted to give the continuous portion of the curve III. In curve VII, V was maintained at 2,500 volts during the first one hour. The discharge was then interrupted for 4 hours and continued again under 2,400 volts·for 80 minutes. In curve XI, V was maintained at 4,000 volts right from the start.

The pressure-time curves VIII, IX, and XI and to a less extent VI and VII, shown in Fig. 2, indicate that a steady and rapid combination of the two gases takes place in the earlier part of the duration of the discharge, and that the reactions later tend towards an equilibrium state, represented by the horizontal shape of the final portion of the curves. The actual time required for the reaction to attain the equilibrium state depends upon several factors, chiefly, the total gas pressure at the start and the applied voltage. Within the scope of the ranges examined in these investigations, it appears from the slopes of curves that lower initial gas pressures and / or higher applied potentials are favourable for a rapid attainment of the final state. This fact is very clearly brought out by the curves IV and XI representing 2,300 and 4,000 volts respectively. It is also to be naturally expected that appreciably lower applied voltages are accompanied by smaller initial rates of reaction, as is borne out by curve X (Fig. 2) obtained for 1,800 volts. Curve VIII (Fig. 2) discloses an important point worthy of note. Observations of the secondary current values which were simultaneously recorded showed that the maximum current flowing through the reaction mixture exactly synchronised with the maximum rate of fall of the gas pressure, noticed at 27'. This last was of course followed by a sudden slowing down of the reaction velocity leading to the steady equilibrium condition. It was also noticed that the characteristic sizzling sound of the discharge became very low and almost inaudible at the 32'-33' interval. Another interesting finding which has resulted from a careful examination of curve IX (Fig. 2) might also be mentioned here ; namely that, on the assumption that the reaction had attained the final equilibrium state at 63' after the start, when the unimolecular velocity constants were calculated from

$$k = \frac{2\cdot303}{t} . \log \frac{a}{a\text{-}x} ,$$

very concordant values for k were obtained. Values of log $(a\text{-}x)$ plotted against the time yielded a straight line graph. Similar results were not obtained for the other cases studied.

. An examination of the variation with time of the secondary current passing through the reaction mixture under a constant applied potential was also made and the curves I, II, III, IV, V shown in Fig. 3 were obtained. While it appears from these that as a result of the progress of the chemical reactions taking place in the ozoniser the magnitude of the secondary current goes on decreasing, for some time at least, with the dura-

tion of the discharge, it is to be noted that the rate of the decrease, unlike that of the gas pressure referred to above, is not quite consistent and is perhaps of a different significance

FIG. 3

Scale A refers to curve G and scale B to curves I to V.

CURVE I (31.5, 2.5, 1800)
CURVE II (24.6, 1.93, 2100)
CURVE III (9.1, 1.94, 2400)
CURVE IV (16.7, 2.15, 2500)
CURVE V (14.7, 2.05, 2100)
G CURVE (16.1, 3.13)
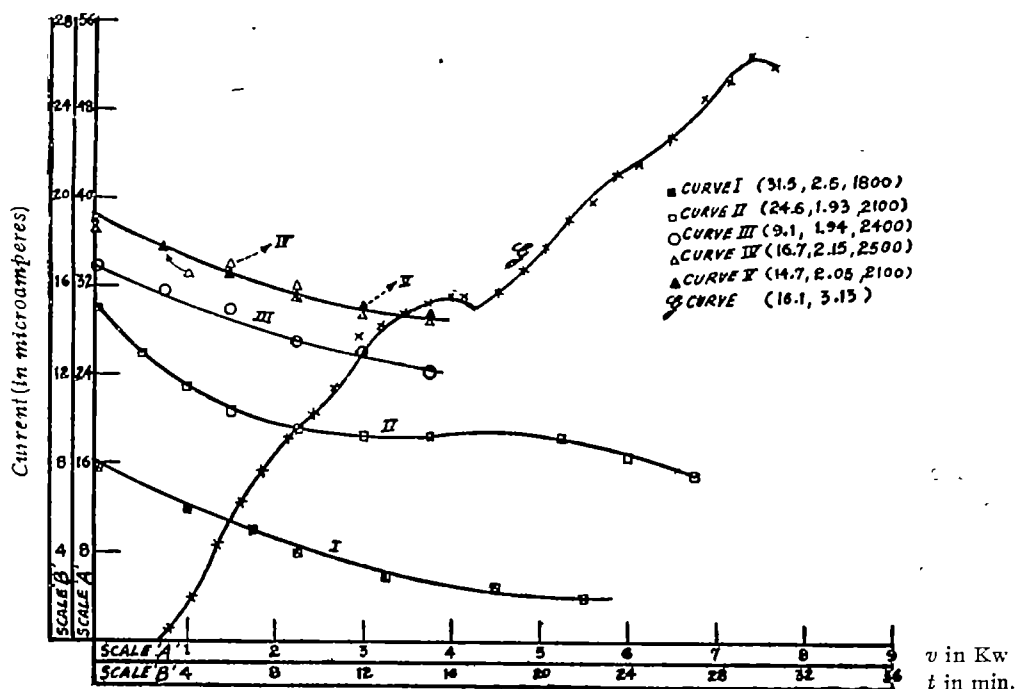
The figures within the brackets indicate the initial gas pressure, p, the $H_2:O_2$ ratio, r, and the applied potential, V, respectively.

altogether. In fact, in certain experiments of this series, it was even found that the current instead of showing a fall in the manner indicated by the curves I to V of Fig. 3, continued to remain more or less at the same value, only fluctuating within narrow limits. Obviously there are several factors contributing to the actual observed values of the current. It is not unlikely that the various direct and reverse reactions involved in the formation and decomposition of water vapour, ozone and hydrogen peroxide side by side constitute factors of considerable complexity detracting from the usefulness of the current measurements for the purpose of studying the reaction-kinetics. Besides, even in the cases where such complicating factors are absent, any attempt at a quantitative study of the chemical kinetics on the basis of the current-measurements seems unwarranted on account of the extraordinary precautions required to be taken in purifying the gases under investigation, in eliminating effectively the role of the last traces of water vapour or other adsorbed gases, etc. Furthermore, the difficulty of accurately controlling the primary voltage within narrow limits for an appreciable period of time stands in the way of maintaining correctly and exactly a constant secondary potential.

The general variation of the secondary current with applied voltage for hydrogen-oxygen mixtures is indicated by the curve G (Fig. 3). Since it was found that the

reactions proceeded with measurable velocities at or below 2,600 volts, higher potentials were not applied in most of these experiments. The initial gas pressures in the different

FIG. 4

x CURVE I (42.0 , 2.13)
o CURVE II (40.4, 1.17)
□ CURVE III (31.5, 2.50)
△ CURVE IV (27.1 , 2.15)
♣ CURVE V (16.7, 2.15)
▲ CURVE VI (16.1, 3.12)
■ CURVE VII (15.5, 2.23)
☆ CURVE VIII (14.7, 2.13)
+ CURVE IX (14.7, 2.05)

Applied potential, V, in volts

The figures within the brackets indicate the total initial gas pressure, p and the $H_2 . O_2$ ratio, r, respectively
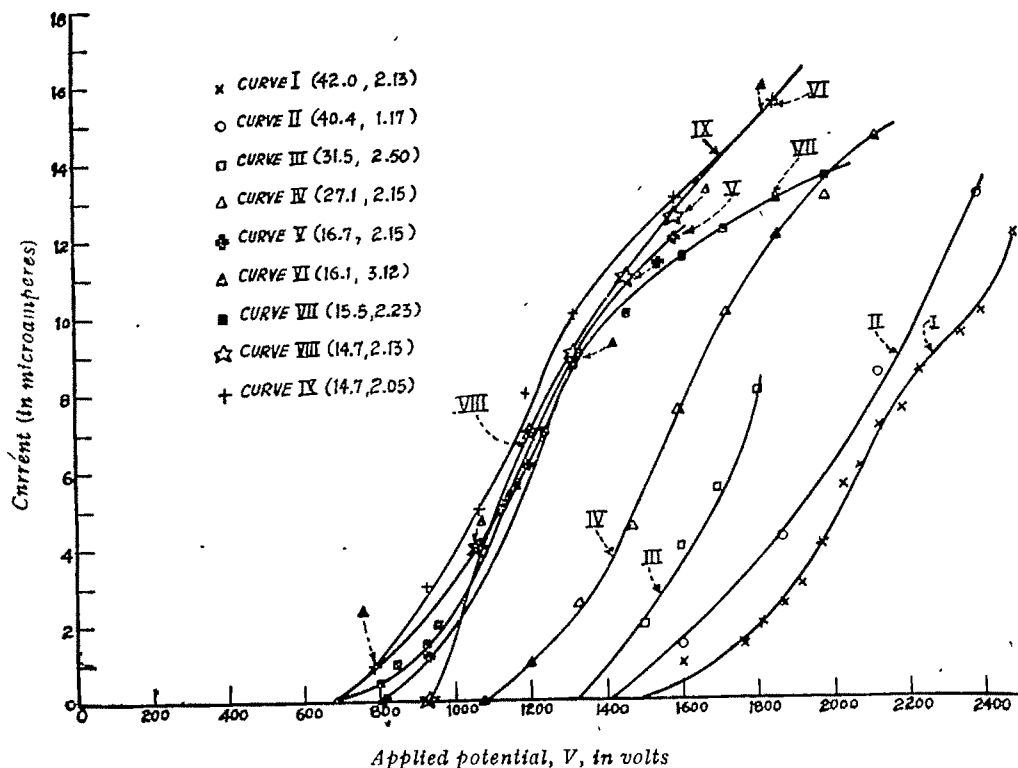
cases ranged from 3 to 50 cm. Hg and the $H_2 : O_2$ ratios were varied from 1 : 1 to 3 : 1. The micro-ammeter readings were noted at each stage and the applied potential was increased and these were plotted against the values of the latter. Some typical curves obtained are shown in Figs. 4 and 5. It will be seen from the curves I, II, III and IV (Fig. 4) which refer to systems of pressure over 27 cm. Hg., that the expected and looked for large and sudden increases of the current values at or near the threshold potentials are not found. At pressures below 27 cm. Hg, while the existence of such a feature is not very clearly noticeable (see curves V to IX of Fig. 4) there is a distinct tendency in that direction. In the case of curves X to XVI of Fig. 5 it is distinctly discernible and it appears to be particularly so at the lowest pressures studied, namely in the range 3·7 to 10 cm. Hg. A discussion of the significance and implications of these results will be made in a separate communication.

A. JOGARÁO

FIG. 5

Applied potential, V, in volts.
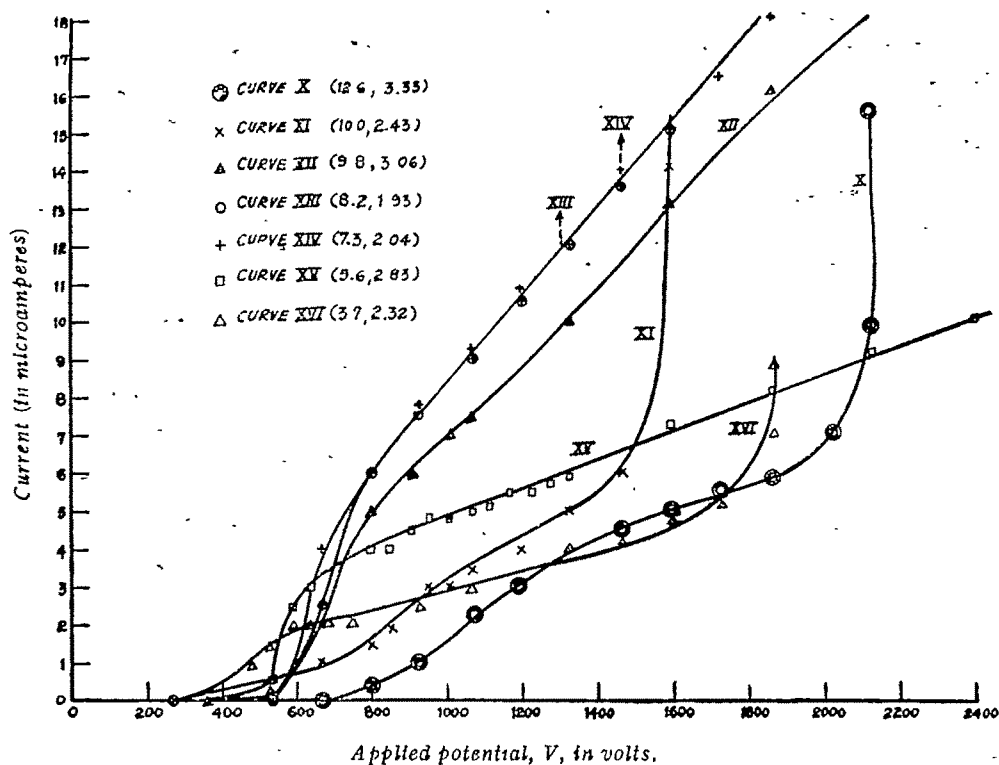
The figures within the brackets indicate the total inititial gas pressure p,
and $H_2 : O_2$ ratio, r, respectively.

The author desires, in conclusion to express his sincere thanks fo Prof. S. S. Joshi, Head of the Department of Chemistry, Benares Hindu University, for suggesting this work and for his kind guidance and interest in this investigation. The laboratory facilities afforded by the Benares Hindu University for conducting this work are also gratefully remembered by the author.

This author's thanks are due to Dr. L. C. Verman, Director Physical Laboratories who gave his kind permission to communicate this paper.

CHEMISTRY OF THE RARE-EARTHS. PART I.
NITRITES OF THE RARE-EARTHS

By. NIHAR KUMAR DUTT

Several series of complex (double and triple) nitrites of the rare-earths, La, Ce, Pa, Nd have been prepared and described. These have been shown to have compositions similar to those for bismuth with which the above-mentioned rare-earth elements have close analogies.

Little is known about the simple nitrites of the rare-earths. They have, however, been utilized in the separations of the yttrium earths from one another (Halden and James *J. Amer. Chem. Soc.*, 1914, **36**, 1418; Hopkins and Balke, *ibid.*, 1916, **38**, 2332) by fractional hydrolysis to insoluble basic nitrites. Only cerous nitrite has been described by Morgan (*J. Chem. Soc.*, 1907, **91**, 476) obtained by double decomposition of equivalent quantities of cerous sulphate and barium nitrite. On evaporating the solution over KOH *in vacuo*, he obtained yellow deliquescent crystals, whose analysis indicated a hydrated cerous nitrite contaminated with a certain proportion of $Ce(OH)_3$.

Some sparingly soluble triple nitrites of the cerium and yttrium earths with alkali metals and bivalent metals like Cu, Ni and Co have been described by Cuttica and Gallo (*Gazzetta*, 1923, **63**, 374). The triple nitrites of cobalt have the general formula $5R^I NO_2$, $2Co^{II}(NO_2)_2$. $R_{III} (NO_2)_3$ where R^I stands for K, Rb or Tl and R^{III} for Ce, La, Pr, Nd and Yt. They are not, truly speaking, complex rare-earth nitrites but cobalto-nitrites of alkali metals having the latter partly substituted by rare-earth metals; hence they may be represented as $[Co(NO_2)_6]_2R_5^IR^{III}$. They are slowly attacked by cold dilute acids yielding $R_3^ICo(NO_2)_6$. The compound $2Co(NO_2)_2$, $Ce(NO_2)_3$, $5KNO_2$ described as a green powder, $2Co(NO_2)_2$, $Ce(No_2)_3$, $5RbNO_2$ also green, and $2 Co (NO_2)_2$, $Ce (NO_2)_3$, $5TlNO_2$ deep brown all behave similarly and are slowly decomposed by water yielding cerous nitrite and cobaltonitrite.

The analogy of bismuth salts with those of cerium earths and up to those of Gd has been beautifully demonstrated by Urbain (*Compt. rend.*, 1903, **137**, 792) based on the isodimorphism of hydrated bismuth nitrates with the rare-earth nitrates and the isomorphism of the double nitrates of bismuth of the type $2M_1(NO_3)_3$, $3M_2(NO_4)_2$, $24H_2O$ where M_1 may be Bi or ΣLa up to Gd and M_2 may be Mg, Zn, Ni, Co or Mn. Sarkar and Goswami (*J. Indian Chem. Soc.*, 1935, **12**, 608) prepared a number of triple nitrites of the general formula $Cs_2NaR(NO_2)_6$ (where R = Ce, La, Pr, Nd, Sm and Gd) analogous to the corresponding bismuth salts. The elements of the yttrium group beyond Gd do not form such nitrites. Like the corresponding bismuth compound, these are sparingly soluble octahedral crystals stable at the ordinary temperature in the solid state. Their aqueous solutions are slowly hydrolysed. These have been used by them as a micro-test for caesium; rubidium and potassium do not interfere.

Following this remarkable observation, the author of the present paper has considered it desirable to undertake a more detailed study of the complex triple nitrites of the rare-earths and prepared several other series of such salts containing Ce, La, Pr and Nd and Na,

K, Li and Tl with a view to accounting for such sharp difference in properties. Several series of double nitrites have also been prepared. Like the bismuthinitrites prepared by Ball and Abram (*J. Chem. Soc.*, 1913, **103**; 2120) these complex nitrites of the rare-earths fall into two groups of which the general formulae are respectively $X_3R(NO_2)_6$ and $X'_2YR(NO_2)_6$ where X stands for Na, K, Tl and X' stands for K, Tl and Rb (Cs), Y for Na and Li and R for Ce, La, Pr and Nd. It has not been possible to prepare the corresponding ammonium salts owing to the unstable nature of concentrated solutions of ammonium nitrite.

Unlike bismuth, double nitrites of rare-earths with sodium nitrite $Na_3R(NO_2)_6H_2O$ have been obtained in the solid state. The existence of the corresponding bismuth compound has been suspected by Ball and Abram (*loc. cit.*) only in solution, for deep orange coloured liquid results when bismuth nitrate is added to a solution of sodium nitrite. This series of the nitrites of the rare-earths, however, is the least stable, quickly decomposing and giving off nitrous fumes and leaving behind rare-earth hydroxides. All attempts to prepare the corresponding lithium salt, however, have been unsuccessful as with the bismuthinitrite.

From a study of the compositions of the triple nitrites of the rare-earths, it is evident that no such compounds exist containing two metals of the same series X' or Y, all attempts to prepare them have also been unsuccessful, yielding only mixtures of the corresponding double nitrites. In this respect, these triple nitrites resemble closely the bismuthinitrites of Ball and Abram.

Of the triple nitrites the salts containing caesium prepared by Sarkar and Goswami (*loc. cit.*) are the least soluble while those containing potassium are the most soluble, the other series having intermediate solubilities.

From a consideration of the above facts, the above mentioned differences in the behaviour of caesium, rubidium and potassium salts can now be explained; for caesium-potassium salts do not exist being metals of the same series X', whereas caesium-sodium salts do so being metals of different series. Again rubidium-sodium and potassium-sodium triple nitrites, though capable of existence, being more soluble (Rb_2-Na salts moderately soluble and K_2-Na highly soluble) than the caesium-sodium triple nitrites, only this latter series of salts being very insoluble ones, are precipitated out from mixtures of the three, the other remaining in solution.

These salts are completely dissociated in solution into their constituent ions, since physico-chemical methods fail to detect the presence of any complex ion in solution. Thermometric and conductometric titrations of solutions of the rare-earth nitrates with alkali nitrites gave no change in temperature and no break in the conductivity curve.

EXPERIMENTAL

All nitrites used must be free from free alkali. Solutions of rare-earth nitrites and thallous and lithium nitrites used throughout the work described in this paper were prepared by the double decomposition between the corresponding sulphates and barium nitrite.

Double Nitrites of the Rare-earths.

1. *Sodium Lanthanum Nitrite.*—Lanthanum nitrite solution as prepared from 5 g. of anhydrous lanthanum sulphate and 7 g. of barium nitrite, was mixed with a solution of

4 g. of sodium nitrite, dissolved in the least quantity of water and the resulting solution was allowed to crystallise in a vacuum desiccator over concentrated sulphuric acid in a refrigerator. After several days, beautiful crystals separated, the crystals were drained under suction, washed first with a sodium nitrite solution (25%), then with 50% aqueous acetone and finally with acetone. They were then dried between folds of the filter paper.

The salt crystallised in large, cream coloured plates, was very unstable, decomposed in a few days giving off nitrous fumes It was highly soluble in water, the aqueous solution decomposing on heating. {Found: Na, 13·68; La, 27·41; NO_2, 54·78. $Na_3La(NO_2)_6H_2O$ requires Na, 13·77; La, 27·54; NO_2, 55·09 per cent}.

2. *Sodium Cerium Nitrite.*—The method of preparation was the same as the preceding salt using cerous sulphate in place of lanthanum sulphate. The salt crystallised in bright yellow plates and in other respects, it resembled very closely the lanthanum salt. {Found : Na, 13·66; Ce, 27·78; NO_2, 54·62. $Na_3 Ce(NO_2)_6H_2O$ requires Na, 13·71; Ce, 27·83; NO_2, 54·87 per cent}.

3. *Sodium Praseodymium Nitrite.*—It was prepared in the same way as above using praseodymium sulphate. The salt separated in beautiful green plates. {Found : Na, 13·52; Pr, 28·02 ; NO_2, 54·42. $Na_3Pr(NO_2)_6H_2O$ requires Na, 13·66 ; Pr, 28·12; NO_2, 54·65 per cent}.

4. *Potassium Lanthanum Nitrite.*—The salt was prepared exactly as the corresponding sodium salt (No. 1) using potassium nitrite in place of sodium nitrite. The salt crystallised in cream-coloured plates. The potassium salt was found to be stabler than the corresponding sodium salt. {Found : K, 21·24; La, 25·21; NO_2, 50·05. $K_3La(NO_2)_6H_2O$ requires K, 21·27 ; La, 25·27 ; NO_2, 50·18 per cent}.

5. *Potassium Cerium Nitrite.*—The method of preparation was similar to above. The salt was obtained in light yellow plates, stabler than the correponding sodium salt. It was highly soluble in water, aqueous solution gradually decomposes. {Found: K, 21·21 ; Ce, 25·38 ; NO_2, 50·05. $K_3Ce(NO_2)_6H_2O$ requires K, 21·23 ; Ce, 25·41; NO_2, 50·09 per cent}.

6. *Potassium Praseodymium Nitrite.*—It was prepared exactly as the previous salt. The salt was obtained in light green plates. It was stabler than the previous one, the dry salt keeps for several days, aqueous solution only slowly decomposes. {Found: K, 21·05; Pr, 25·53; NO_2, 49·78. $K_3Pr(NO_2)_6H_2O$ requires K, 21·15 ; Pr, 25·68 ; NO_2, 50·06 per cent}.

7. *Potassium Neodymium Nitrite.*—The method of preparation was very similar to the above. The salt crystallised in light red plates. In stability and other properties it resembled the praseodymium salt. {Found : K, 21·02; Nd, 25·55; NO_2, 49·68. $K_3Nd(NO_2)_6H_2O$ requires K, 21·14 ; Nd, 25·68 ; NO_2 49·91 per cent}.

8. *Thallium Lanthanum Nitrite.*—This series of salts containing thallium was stabler and less soluble' than the other series containing sodium or potassium. The salt was obtained from thallium nitrite and lanthanum nitrite. Due to its lesser solubility in water it was easier to prepare being separated from a less concentrated solution than the previous ones. The salt was obtained in light orange plates, less soluble and stabler than the corresponding sodium and potassium salts. {Found : Tl, 58·45 ; La, 13·05 ; NO_2, 26·32. $Tl_3La(NO_2)_6H_2O$ requires Tl, 58·62 ; La, 13·22 ; NO_2, 26·44 per cent}.

9. *Thallium Cerium Nitrite.*—The method of preparation was the same as in the previous one. In crystalline form and other properties, it resembled the lanthanum salt

in all respects. {Found: Tl, $58\bar{6}1$: Ce, $13\cdot35$; NO_2, $26\cdot17$; $Tl_3Ce(NO_2)_6H_2O$ requires Tl, $58\cdot51$. Ce, $13\cdot38$; NO_2, $36\cdot38$ per cent}.

10. *Thallium Praseodymium Nitrite.*—The method of preparation was the same as above. It crystallised in greenish yellow plates; in other properties it resembled the previous ones. {Found: Tl, $58\cdot32$; Pr, $13\cdot39$; NO_2, $26\cdot25$. $Tl_3Pr(NO_2)_6H_2O$ requires Tl, $58\cdot45$; Pr, $13\cdot47$; NO_2 $26\cdot36$ per cent}.

11. *Thallium Neodymium Nitrite.*—It was prepared exactly as the previous one. {Found: Tl, $58\cdot32$; Nd, $13\cdot52$; NO_2, $26\cdot21$. $Tl_3Nd(NO_2)_6H_2O$ requires Tl, $58\cdot40$; Nd, $13\cdot55$; NO_2, $26\cdot33$ per cent}.

Triple Nitrites of the Rare-earths.

The triple nitrites are, in general, less soluble and more stable than the double nitrites of the rare-earths; the most stable and the least soluble being the series $Cs_2NaR(NO_2)_6$ previously described by Sarkar and Goswami (*loc. cit.*). Consequently, they are easier to prepare. They can be kept unaltered for months together. They crystallise in octahedral forms differing in this respect from the double nitrites.

1. *Potassium Sodium Lanthanum Nitrite.*—To a solution of lanthanum nitrite, obtained from 5 g. of anhydrous lanthanum sulphate and 7 g. of barium nitrite, were added a solution of $3\cdot5$ g. of potassium nitrite and $1\cdot5$ g. of sodium nitrite and the resulting solution allowed to crystallise in a vacuum desiccator kept in the refrigerator. After two or three days, beautiful crystals separated out. The crystals were drained under suction, washed first with aqueous acetone and finally with pure acetone. The salt crystallised in cream coloured octahedral form. It is moderately soluble in water, the aqueous solution gradually decomposing giving off nitrous fumes. {Found: K, $15\cdot01$; Na, $4\cdot32$; La, $26\cdot38$; NO_2, $53\cdot36$. $K_2NaLa(NO_2)_6$ requires K, $15\cdot12$; Na, $4\cdot46$; La, $26\cdot94$; NO_2, $53\cdot49$ per cent}.

2. *Potassium Sodium Cerium Nitrite.*—The salt was prepared in the same way as above taking cerous sulphate in place of lanthanum sulphate. The salt was obtained in light yellow octahedral crystals; in other respects it resembled the above salt. {Found: K, $14\cdot97$; Na, $4\cdot41$; Ce, $27\cdot01$; NO_2, $53\cdot13$. $K_2NaCe(NO_2)_6$ requires K, $15\cdot08$; Na, $4\cdot45$; Ce, $27\cdot08$; NO_2, $53\cdot38$ per cent}.

3. *Potassium Sodium Praseodymium Nitrite.*—The method of preparation was similar to above. The salt is obtained in pale green octahedral crystals. It is stabler than the previous salts. {Found: K, $14\cdot88$; Na, $4\cdot25$; Pr, $27\cdot08$; NO_2, $53\cdot05$. $K_2NaPr(NO_2)_6$ requires K, $15\cdot03$; Na, $4\cdot43$: Pr, $27\cdot36$; NO_2, $53\cdot18$ per cent}.

4. *Potassium Lithium Lanthanum Nitrite.*—The salt was prepared in the same way as salt No. 1 by taking lithium nitrite (1 mol.) in place of sodium nitrite. It separated in cream coloured octahedral crystals. The salt was less stable than the potassium-sodium salt, easily decomposed with water and could not be kept for a long time. {Found: K, $15\cdot48$; Li, $1\cdot32$; La, $27\cdot68$; NO_2, $54\cdot95$. $K_2LiLa(NO_2)_6$ requires K, $15\cdot60$; Li, $1\cdot40$; La, $27\cdot70$; NO_2, $55\cdot20$ per cent}.

5. *Potassium Lithium Cerium Nitrite.*—The method of preparation was the same as above. The salt separated in yellow crystals. {Found: K, $15\cdot49$; Li, $1\cdot35$; Ce, $27\cdot83$; NO_2, $54\cdot85$. $K_2LiCe(NO_2)_6$ requires K, $15\cdot59$; Li, $1\cdot40$; Ce, $27\cdot95$; NO_2, $55\cdot09$ per cent}.

6. *Potassium Lithium Praseodymium Nitrite.*—The salt was prepared in the same way as above. It separated in pale green octahedral forms. {Found : K, 15˙42 ; Li, 1˙30 ; Pr, 28˙12 ; NO_2, 54˙65. $K_2LiPr(NO_2)_6$ requires K, 15˙51 ; Li, 1˙39 ; Pr, 28˙23 ; NO_2, 54˙87 per cent}.

7. *Thallium Sodium Lanthanum Nitrite.*—This series of salts containing thallium was much stabler than the potassium-sodium or potassium-lithium compounds. The stability was perhaps due to the bigger mass of the thallium ion. For the same reason, compounds containing rubidium and caesium were stabler than the rest. The salts were also less soluble than the previous ones. The salt was prepared by evaporating, in a desiccator a solution containing two equivalents of thallium nitrite, one of sodium nitrite and one of lanthanum nitrite.

The salt separated in light yellow octahedral crystals. It was moderately soluble in water, rather stable and when dry it could be kept for a long time. {Found : Tl, 48˙11 ; Na, 2˙62 ; La, 16˙31. NO_2, 32˙45 ; $Tl_2NaLa(NO_2)_6$ requires Tl, 48˙25 ; Na, 2˙72 ; La, 16˙43 ; NO_2, 32˙62 per cent}.

8. *Thallium Sodium Cerium Nitrite.*—The salt was prepared in the same way as above. It separated in orange octahedron. {Found : Tl, 48˙08 ; Na, 2˙65 ; Ce, 16˙48 ; NO_2, 32˙48. $Tl_2NaCe(NO_2)_6$ requires Tl, 48˙22; Na, 2˙71; Ce, 16˙51; NO_2, 32˙55 per cent}.

9. *Thallium Sodium Praseodymium Nitrite.*—It was prepared exactly as the other salts. The triple salt was obtained in the form of light greenish yellow octahedral crystals. {Found : Tl, 47˙85 ; Na, 2˙65 ; Pr, 16˙56 ; NO_2, 32˙35. $Tl_2NaPr(NO_2)_6$ requires Tl, 48˙05 ; Na, 2˙71 ; Pr, 16˙72 ; NO_2, 32˙51 per cent}.

10. *Thallium Sodium Neodymium Nitrite.*—The method of preparation was the same as above. {Found : Tl, 47˙78 ; Na, 2˙68 ; Nd, 16˙66 ; NO_2, 32˙42. $Tl_2NaNd(NO_2)_6$ requires Tl, 48˙05 ; Na, 2˙71 ; Nd, 16˙75 ; NO_2, 32˙51 per cent}.

11. *Thallium Lithium Lanthanum Nitrite.*—The method of preparation was the same as above substituting lithium nitrite in place of sodium nitrite. {Found : Tl, 48˙95 ; Li, 0˙76 ; La, 16˙66 ; NO_2, 33˙06. $Tl_2LiLa(NO_2)_6$ requires Tl, 49˙16 ; Li, 0˙84 ; La, 16˙75; NO_2, 33˙25 per cent}.

12. *Thallium Lithium Cerium Nitrite.*—It was prepared in the same way as above. The salt separated in deep orange crystals. In other respects it resembled the other thallium salts. {Found : Tl, 48˙86 ; Li, 0˙78 ; Ce, 16˙66 ; NO_2, 32˙88. $Tl_2LiCe(NO_2)_6$ requires Tl, 49˙15 ; Li, 0˙84 ; Ce, 16˙83 ; NO_2, 33˙18 per cent}.

13. *Thallium Lithium Praseodymium Nitrite.*—The method of preparation was the same as above. {Found : Tl, 48˙76 ; Li, 0˙80 ; Pr, 16˙92 ; NO_2, 32˙88. $Tl_2LiPr(NO_2)_6$ requires Tl, 48˙94 ; Li, 0˙84 ; Pr, 17˙05 ; NO_2 33˙13 per cent}.

14. *Thallium Lithium Neodymium Nitrite.*—The salt was prepared exactly as the praseodymium salt, which it resembled in all respects. {Found : Tl, 48˙48 ; Li, 0˙86 ; Nd, 16˙88 ; NO_2, 33˙25. $Tl_2LiNd(NO_2)_6$ requires Tl, 48˙95 ; Li, 0˙84 ; Nd, 17˙05 ; NO_2, 33˙13 per cent}.

15. *Rubidium Sodium Lanthanum Nitrite*—Next to caesium-sodium compounds, these rubidium-sodium salts were the least soluble of all the triple nitrites studied. These could be prepared by methods similar to that for cesium-sodium compounds. Only more concentrated solutions were required. To 5 c.c. of 70% solution of lanthanum nitrate

were added 5 c.c. of 70% sodium nitrite solution, and the mixture was cooled in ice and filtered from any sodium nitrate deposited. To the filtrate was then added 1 c.c. of 50% solution of rubidium nitrate and kept for some time. The cream coloured crystals were then filtered under suction from mother-liquor as much as possible, washed first with 50% sodium nitrite solution, then with 50% acetone and finally with acetone. The salt separated in cream coloured octahedral crystals. {Found : Rb, 28·06 ; Na, 3·81 ; La, 22·72 ; NO_3, 45·11. $Rb_2NaLa(NO_2)_6$ requires Rb, 28·08 ; Na, 3·78 ; La, 22·82 ; NO_2, 45·32 per cent}.

16 *Rubidium Sodium Cerium Nitrite.*—The salt was prepared exactly as the previous one, which it resembled in all respects. {Found : Rb, 27·88 ; Na, 3·82 ; Ce, 23·01 ; NO_2, 45·06 $Rb_2NaCe(NO_2)_6$ requires Rb, 28·03 ; Na, 3·77 ; Ce, 22·85 ; NO_2, 45·24 per cent}.

17. *Rubidium Sodium Praseodymium Nitrite.*—The method of preparation was the same as above. The salt separated in green octahedral crystals. In all other respects it resembled the above two salts. {Found : Rb, 27·72 ; Na, 3·91 ; Pr, 22·95 ; NO_2, 45·02. $Rb_2NaPr(NO_2)_6$ requires Rb, 28·00 ; Na, 3·76 ; Pr, 23·08 ; NO_2, 45·17 per cent}.

Method of Analysis.

The salts were decomposed with concentrated hydrochloric acid and the rare-earths were precipitated as hydroxides by double precipitation with ammonia. The precipitated hydroxides were filtered, dissolved in dilute nitric acid and precipitated as oxalates. They were then ignited and weighed as oxides. From the filtrate ammonium salts were removed and the total alkali metals were weighed in the form of chlorides. Potassium was estimated as perchlorate and sodium or lithium, as the case may be, was determined by difference. In salts containing thallium, the total thallium and alkali metals were weighed as sulphates. Thallium was estimated as thallium iodide and the alkali metals sodium and lithium were obtained by difference. Nitrogen was estimated by conversion to ammonia by distillation with zinc and alkali and subsequent absorption in standard acids.

CHEMISTRY OF THE RARE-EARTHS. PART II.
MACRO- AND MICRO-ESTIMATION OF CAESIUM IN PRESENCE OF POTASSIUM AND RUBIDIUM WITH THE HELP OF RARE-EARTHS

By Nihar Kumar Dutt

An improved method for the quantitative determination of caesium and its separation from rubidium and potassium has been described. Cs has been precipitated as $Cs_2NaLa(NO_2)_6$ and weighed directly in a gooch crucible. Cs has also been determined volumetrically by estimating the nitrite content of the compound with ceric sulphate. Both gravimetric and volumetric processes have been successfully adopted for micro-determination of caesium.

The close similarity in the chemical behaviour of potassium, rubidium and caesium is well known. Their separation from one another is an important problem in analytical chemistry. Various attempts have been made in this line, but none of the methods appear to be quantitative.

The best known complex salt at present in use for the estimation of caesium is the compound $4CsCl$, $4SbCl_3$, $FeCl_3$, (Godeffroy, *Ber.*, 1874, **7**, 374; Strecker and Diaz, *Z. anal. Chem.*, 1925, **67**, 321; Moser and Ritschel, *ibid.*, 1927, **70**, 184) the method being quantitative only under conditions which cause appreciable co-precipitation of rubidium. Various organic acids have been tried but with little success.

O'Leary and Papish (*Ind. Eng. Chem. Anal. Ed.*, 1934, **6**, 107) developed an improved method for the quantitative determination and separation of potassium, rubidium and caesium based on the use in succession of 9-phosphomolybdic acid, silicotungstic acid and chloroplatinic acid. They observed that rubidium and caesium salts of the first named acid are insoluble, potassium salt being perfectly soluble. The caesium salt of silicotungstic acid is insoluble in $6N$ hydrochloric acid, rubidium salt being soluble. According to the authors "the method proposed does not afford the clean cut sharpness of separation that is desirable though it is much more reliable than those hitherto proposed. The average error introduced in course of the analysis by this method is 2%."

Sarkar and Goswami (*J. Indian Chem. Soc.*, 1935, **12**, 608) while preparing the triple nitrites of the rare-earths of the series $Cs_2NaR(NO_2)_6$ (where R = Ce, La, Pr, Nd, Sm, Gd) observed that these nitrites furnish a delicate microchemical test for caesium, the limit of identification being 4×10^{-8}g.(0·04γ). The test appears to be specific for caesium ; rubidium and potassium do not interfere. It appears to be more sensitive than the triple caesium-silver-gold chloride test advocated by Emich (*Monatsh*, 1918, **39**, 775).

It has been observed by the present author that caesium is quantitatively precipitated as $Cs_2NaLa(NO_2)_6$ from its solution and that the filtrates from such precipitations always yield a negative reaction with perchloric acid, and a method has been developed for the quantitative determination of caesium and its separation from rubidium and potassium in one operation. The precipitate can be directly weighed in a gooch crucible. The compound contains 37·77% of Cs. The metal can also be determined volumetrically by estimating the nitrite content of the compound with ceric sulphate. It has been observed that even 3 mg. of caesium can be estimated accurately. The accuracy of the method has been found to be ±0·2%.

Experimental

Preparation of the reagent.—For reagent, a solution of sodium-lanthanum nitrite is used. A 50% solution of lanthanum nitrate was added to an equal volume of a 50%

solution of sodium nitrite. The solution was then filtered and preserved in a well-stoppered bottle. The solution should be filtered before use if found turbid due to slight decomposition with formation of basic salts.

Preparation of the standard solutions of the Alkali-Salts : Potassium, Rubidium and Caesium.—The alkali salts were taken in the form of their nitrates. Rubidium and caesium nitrates were from Kahlbaum & Co., and potassium nitrate, from Merck & Co., U.S.A. The spectrum of rubidium salt was found to be free from any caesium line when viewed through a direct vision spectroscope and *vice-versa*.

All solutions were made from conductivity water and standardised by the perchloric acid method after being converted into chloride by repeated evaporation with concentrated hydrochloric acid.

Solubility of the compound in Different Solvents.—The compound being moderately soluble in cold water, could not be washed with it. Even in 80% aqueous acetone, the compound was appreciably soluble, whereas sodium nitrite, the impurity to be removed, was practically insoluble in this solvent. Ethyl alcohol also behaved very similarly but the compound was found to be practically insoluble in methyl alcohol and in this solvent, sodium nitrite was known to be soluble to the extent of 4%.

Methyl alcohol was therefore used in the following experiments as wash-liquid after removing the mother-liquor with the help of a few drops of cold saturated solution of sodium nitrite.

Estimation of Caesium.—The solution was evaporated to dryness on the water-bath and redissolved in the least quantity of water. It was then cooled in ice and 3 to 5 c.c. of the reagent depending on the amount of caesium taken, were then added with stirring. The solution was allowed to stand for sometime, then filtered in a weighed gooch crucible, washed first with a few drops of cold saturated solution of sodium nitrite then with ice-cold methyl alcohol and finally with ether. The crucible was then dried in a vacuum desiccator over concentrated sulphuric acid and the caesium weighed as $Cs_2NaLa(NO_2)_6$ (Cs = 37·77%). The results are given in Table I.

Estimation of Caesium in presence of Rubidium.—The method is identical with the one described. The rubidium was estimated in the filtrate as perchlorate after separation of lanthanum by double precipitation with ammonia and removal of ammonium salts by ignition. The results are shown in Table II.

TABLE I		TABLE II			
Cs taken.	Cs found.	Cs taken.	Rb taken.	Cs found	Rb found.
0·05158 g.	0·05165	0·05158 g	0·04658 g.	0·05154 g.	0·046·8 g.
0·02579	0 02583	0·02579	0·05823	0 02575	0·05823
0·00516	0·00514	0·01032	0·05237	0·01034	0·05236
0 02579	0 02575	0·00259	0 02612	0 00261	0·02614
0·03868	0·03864	0·01032	0·2429	0·01034	0 2428

The method worked excellently for mixtures containing rubidium chloride up to 25 times the amount of caesium chloride present. With more rubidium, results were rather high due to co-precipitation of the corresponding rubidium compound.

Estimation of Caesium in presence of Potassium.—The procedure was identical with the previous one. Potassium was estimated in the filtrate as perchlorate after the usual separation of the rare-earth. The results are shown in Table III.

TABLE III				TABLE IV	
Cs taken.	K taken.	Cs found.	K found.	Cs taken.	Cs found.
0·05158 g.	0·05068 g.	0·05158 g.	0·05066 g.	0·05158 g.	0·05160 g.
0·01032	0·10136	0·01034	0·10136·	0·02579	0·02582
0·01032	0·2506	0·01030	0·2507	0·01032	0·01036
0·00258	0 1267	0·00257	0·12625	0·02579	0·02573
0·00516	0·5068	0·00519	0·50683		

The corresponding potassium compound $K_2NaLa(NO_2)_6$ was highly soluble in water and the method worked satisfactorily for mixtures containing potassium up to 100 times the amount of caesium present.

Volumetric determination of Caesium.—As pointed out, caesium may be precipitated as the triple nitrite and estimated by determining the nitrite volumetrically with ceric sulphate.

The method for precipitating, filtering and washing was the same as with the gravimetric method. In a 400 c.c. beaker was taken a measured volume of acidified standard ceric sulphate solution diluted with five times as much water. The precipitate along with the gooch was placed in the beaker under solution and stirred till the precipitate dissolved completely. The excess of cerric sulphate was then titrated with standard ferrous sulphate solution using ferroin (*o*-phenanthroline-ferrous complex) as an internal indicator (1 c.c. of 0·1N $Ce(SO_4)_2 = 0·002216$ g. of Cs). (Table IV)

Interfering Ions.—Anions like oxalate, phosphate, fluoride, etc., which form insoluble salts with rare-earth must be absent. Since bivalent cations like Cu, Co, Ni form some insoluble complex nitrites containing rare-earths (*cf.* Cuttica and Gallo, *Gazzetta*, 1923, **53**, 374) all these ions must be absent.

Micro-estimation.

The same solutions of the alkali salts and the reagent that were used in the macro-determinations, have been used here. Standard solutions were measured out from a micro-burette. All solutions and wash liquids were prepared from conductivity water.

Estimation of Caesium.—The solution was taken in a micro-beaker kept in another small beaker, evaporated to dryness on the water-bath and the residue redissolved in the least quantity of water. It was then cooled in ice and 0·5 to 1·5 c.c. of the reagent, depending upon the amount of caesium taken, was added, one drop at a time, gently rotating the beaker by the hand after the addition of each drop of the reagent. The precipitate was allowed to settle and collected on one side of the beaker. The supernatant liquid was then drawn off through Emich's asbestos packed filter-stick, and the precipitate sucked as dry as possible. Care should, however, be taken that no precipitate entered the filter stick before the filter washing was complete, as the fine pecipitate often choked the filter thereby delaying filtration. It was then washed 5 to 6 times with ice-cold methyl alcohol using 0·25 to 0·5 c.c. for each washing, then once or twice with cold ether and finally dried in a vacuum desiccator over concentrated sulphuric acid, the empty beaker and the filter-stick having been dried similarly. The beaker with the precipitate and the filter-stick was then weighed in the micro-balance after taking the usual precautions of wiping with moist flannel and dry chamois respectively. Some of the results of analysis appear below in Table V.

3—1547P—3

Estimation of Caesium in presence of Rubidium.—The same procedure was followed as already described. Results of analyses are given in the table below (Table VI).

TABLE V		
Cs taken.	Reagent.	Cs found.
1·289 mg.	1·0 c.c.	1·295 mg.
0·644	0·5	0·648
1·031	1·0	1·030
1·289	1·0	1·278

TABLE VI

Vol. of reagent used = 1·5 c.c.

Cs taken.	Rb taken.	Cs found.
1·031 mg.	1·00 mg.	1·040 mg.
1·031	2·50	1·036
1·031	5·10	1·028
1·289	32·50	1·294
1·031	10·50	1·035

Estimation of Caesium in Presence of Potassium.—The procedure was the same as described in the previous cases. Table VII gives some of the results of analysis.

TABLE VII			
Cs taken	K taken.	Reagent.	Cs found.
0·943 mg.	1 00 mg.	1·0 c.c.	0·952 mg.
0·943	10·00	1·5 c c.	0·948
0·943	20·00	,,	0·949
1·257	62·00	,,	1·266
1·257	130·00	,,	1·249

TABLE VIII			
Cs taken	Vol. (cor. for $N/50$ ceric sulphate).	Vol. reqd.	Cs found.
1·257 mg.	2·856 c c.	2·837 c c.	1·265 mg
1·289	2·922	2 909	1·295
0·943	2·145	2·129	0·950
0·043	2·122	2·129	0·940
1·031	2·327	2·3273	1·028

The corresponding potassium compound $K_2NaLa(NO_3)_6$ being highly soluble in water, the method worked satisfactorily for mixtures containing potassium upto 100 times the amount of caesium present.

Volumetric estimation of Caesium.—The estimation of caesium by determining the nitrite volumetrically with ceric sulphate, was also employed successfully for the micro-estimation of the same.

The method for precipitating, filtering and washing was the same as with the gravimetric method. A known volume 3 to 4 c.c. of the standard ceric sulphate ($N/50$) in dilute sulphuric acid was taken from a micro-burette in the micro-beaker containing the precipitate and the filter-stick. Water (1-2 c.c.) was added to dip the stick above the constriction under solution. It was then warmed on a water-bath for a few minutes till the precipitate was completely dissolved. It was then cooled to room temperature and the excess of ceric sulphate was titrated with standard ferrous sulphate ($N/50$) using ferroin as an internal indicator (1 c.c. $N/50$ ceric sulphate = 0·443 mg. of Cs). Results are in Table VIII.

Indicator correction.—With ceric sulphate and ferroin when the standard titrating solution was sufficiently dilute, indicator correction is essential. The correction has been found to obey a linear variation and is almost exactly equal 0·2 c.c. of $N/50$-ceric solution for every 0·05 c.c. of ferroin added.

The author's best thanks are due to Dr. P. B. Sarkar for his kind interest and all laboratory facilities.

CHEMISTRY OF THE RARE-EARTHS. PART III.
ESTIMATION OF RARE-EARTHS IN URANIUM MINERALS

By Nihar Kumar Dutt

A critical re-examination of the various methods for the above separation has been made. The method with the help of ether has been improved upon and made suitable for an accurate separation of the rare-earths from excess of uranium.

The problem of the separation of rare-earths and thorium from uranium is of considerable interest for the analysis of uranium minerals like uraninite, pitch blende, etc. In such minerals, the ratio of uranium : rare-earth may be as high as 200. The methods in common use do not afford the clean cut sharpness of separation that is desirable. Though rare-earths can be precipitated quantitatively from acid solution with oxalic acids, the presence of large quantity of uranium has some solvent action on it due to the formation of some complex oxalates. Precipitation of rare-earths in slightly acid solution with ammonium oxalate in presence of salicylic acid, which has been found to form some complex with uranium, has been tried by Canneri and Fernandes (*Gazzetta*, 1924, **54**, 770). Hydroxylamine method of Jannasch and Schilling (*J. prakt. Chem.*, 1905, **72**, ii, 26) gives good results, but the method seems to be tedious since in the filtrate hydroxylamine must be removed before proceeding with the estimation of uranium. The classical reagent for the above separation is hydrofluoric acid used by Lawrence-Smith. Various contradictory results are recorded in the literature for the above separation with the help of ether, the principal reason for this deviation being that dried rare-earths and thorium nitrates have some solubility in anhydrous ether. From a study of the ternary system uranium nitrate—thorium nitrate—ether, it has been shown by Misciattelli (*Phil. Mag.*, 1929, **7**, 670) that above 20°, when the ether is saturated with uranium nitrate (which requires 8% of the nitrate), dried thorium nitrate is quite insoluble in it.

A critical review of the various methods for the above separation has been made in the present communication. The method with ether has been developed for the separation of rare-earths from uranium.

Experimental

Preparation of standard solutions.—Uranium nitrate, thorium nitrate and rare-earth of 'Kahlbaum' were used. All solutions were standardised by taking an aliquot part and evaporation to dryness and subsequent ignition to oxide. The ether used was purified in the usual manner and dried over metallic sodium.

Oxalic Acid Method.

Thorium can be separated from uranium accurately with oxalic acid even when the ratio U/Th is 200. Rare-earths can only thus be separated when the ratio of U : R.E. is <25. For higher percentage of uranium the result is always low due to the solvent action as stated above.

TABLE I			TABLE II			
Separation of uranium and thorium.			*Separation of uranium and rare-earth.*			
ThO₂ taken.	Ratio UO₃ : ThO₂.	ThO₂ found.	Rare-earth taken.	Ratio UO₃ · R₂O₃.	R₂O₃ found.	%Error
0·1244 g.	5	0·1240 g.	0·0543 g.	5	0·0545	—
0·1244	10	0·1240	0·0543	10	0·0543	—
0·1244	25	0·1243	0·0543	25	0·0541	—
0·1244	50	0·1240	0·0543	50	0·0481	7
0·0622	200	0·0618	0·0543	100	0·0426	24

Hydroxylamine Method.

In presence of hydroxylamine, uranium hydroxide is not precipitated by ammonia while rare-earths and thorium are thus precipitated. This method of Jannasch and Schilling (*loc. cit.*) works well up to the limit when uranium is even 100 times that of rare-earths.

TABLE III				TABLE IV		
Rare-earths taken.	Ratio.	Rare-earths found.	Rare-eartns taken	Ratio.	Rare-earths found.	%Error.
0·1060 g.	10	0·1061 g.	0·0543 g.	5	0·0543 g.	—
0·0530	50	0 0531	0·0543	10	0·0545	—
0·0212	75	0·0211	0·0543	25	0·0542	—
0·0212	100	0·0212	0·0543	50	0·0522	4
			0·0543	100	0·0505	7

Salicylic Acid Method.

This method works well only when the above ratio is lower than 25. With higher percentages of uranium much error is introduced (Table IV).

Hydrofluoric Acid Method.

This method has been used by various workers for the analysis of radio-active minerals. Though this method has been found to work well, it seems to be time-consuming due to the fact that the precipitated fluoride should be decomposed with concentrated sulphuric acid and the anhydrous sulphate should be dissolved in ice water (Table V).

TABLE V			TABLE VI		
Rare-earths taken.	Ratio.	Rare-earths found.	Rare-earths taken.	Ratio.	Rare-earths found.
0·0270 g.	25	0·0271 g.	0·0440 g.	100	0·0443 g.
0·0270	50	0·0270	0·0210	200	0·0219
0·0135	100	0·0135	0 0220	400	0·0220

Separation with the help of Ether.

A method based on the use of ether for the separation of rare-earths from uranium has been developed. The principle underlying the method is based on the fact that uranium need not be completely removed before precipitating rare-earths but presence of uranium to the extent of 25 times that of rare-earths does not interfere in the quantitative precipitation of the latter as has been shown by us. And so long as the ether is saturated with uranium nitrate, no rare-earth nitrate goes into solution. Similar observation with thorium nitrate has been made by Misciattelli (*loc. cit.*). Hence by completely drying all the nitrates and also ether and adjusting the volume of ether it has been possible to remove the main bulk of the uranium nitrate present without dissolving any rare-earth nitrate. The residue left is freed from ether, dissolved in water and is then precipitated with oxalic acid as usual, the uranium nitrate left behind with it, does not interfere. This method has been found to work well even when the amount of uranium in the original sample is 400 times that of rare-earths (Table VI.)

The author's best thanks are due to Dr. P. B. Sarkar for his kind interest and all laboratory facilities.

HETEROGENEOUS EQUILIBRIA: THE TERNARY SYSTEM OF POTASSIUM NITRATE, AMMONIUM NITRATE AND WATER

By RAM CHAND AND JANESH CHANDRA JAIN

Ammonium nitrate cannot be separated in pure state from solutions containing even small quantities of potassium nitrate while potassium nitrate can be separated in a pure state when its concentration in the solutions is more than 25%.

The ternary system of potassium nitrate, ammonium nitrate and water has been studied by Bahl and Singh (*J. Indian Chem. Soc.*, 1940, **17**, 441) who report that both the salts can be separated out in the pure state from mixtures of the two, there being no formation of mixed crystals. While working on the reversible salt pair system of ammonium nitrate, potassium sulphate and water it was found that the ternary system reported above required a fresh investigation.

Isothermal relationships have been investigated at 25°. At this temperature exploration was carried out by means of Schrienemakers's well known 'residue method'. Owing, however, to the formation of solutions this method was not sufficient to fix the composition of the solid phases with certainty. Supplementary experiments for isolation and analysis of the solid phases were carried out.

EXPERIMENTAL

Experiments were conducted in a thermostat maintained at 25° ±0·05° with the help of an electrical thermoregulator. Definite proportions of the two salts were mixed with water, sealed in bulb tubes and then shaken for 48 hours. The seals were then broken and the solution separated from the solid with the help of pipettes heated to 25°. Both the solid and the liquid were analysed separately.

For supplementary examination of solid phases, solutions were allowed to evaporate at the temperature of the thermostat until a small crop of crystals appeared. The crystals were separated under suction on a sintered glass funnel placed in a hot water funnel through which water at 25° was being circulated and they were washed with little water and dried rapidly on filter paper pads.

Ammonium nitrate was estimated by determining the quantity of ammonia in the solution by distilling with alkali. Potassium nitrate was determined by finding out total nitrate by ferrous sulphate method, being frequently checked against Lunge's nitrometer method, and after subtracting the nitrate for ammonium nitrate the quantity of patassium nitrate was calculated. Water was always estimated by difference.

The composition of the solutions and wet solids obtained by Schreinemakers's method are presented in the following table.

The points representing the solubilities of pure ammonium nitrate and potassium nitrate in water are taken from Seidells' 'Dictionary of Solubilities.'

These results are plotted graphically on the triangular co-ordinate system in Fig. 1.

The results show clearly that pure ammonium nitrate does not separate out from solutions containing even very small quantities of potassium nitrate, while potassium nitrate separates out in a pure state from solutions containing more than 25% of potassium nitrate. It is surprising that the formation of mixed crystals in this system was missed by Bahl and Singh (*loc. cit.*). This is evidently due to the fact that they have tried only 5 compositions and thus ignored some vital points. The results have been confirmed by isothermal evaporation of solutions rich in ammonium nitrate. The base of the triangular co-ordinate diagram is formed of the binary system NH_4NO_3-KNO_3 which has been studied very

TABLE I

System NH₄NO₃, KNO₃ and water.   Composition by weight.

Solution				Rest		Solid
H₂O	KNO₃	NH₄NO₃	H₂O	KNO₂	NH₃NO₃	NH₄NO₃
31·90%	.	68·10%	...	...	...	
32·14	1·742%	66·12	23·19%	2·606%	74·20%	
31·66	3·714	64·63	20·17	4·773	75·06	
31·48	6·288	62 23	21·25	10·880	80 87	
31·76	6 640	61 59	23·09	8·860	68·05	
31·90	8 870	59 22	17 97	13 78	68·24	
31 04	12·25	56 70	19·35	17·60	63·05	Mixed crystals
31 16	13·03	55 81	20·64	18·06	61·30	
31·20	16 62	52·18	16·13	33·60	50·27	
31 49	17·72	50·79	18·88	35·03	46·09	
31·42	17 82	50·76	17·10	35·56	47·34	
31·07	18·66	50·27	22 99	27·62	49·39	
32·40	19·00	48·60	18·00	51 00	31·00	
38·25	19·18	41·94	22 14	53·47	24·39	
41·60	20·32	38 08	21·20	56·53	22·27	KNO₃
43·25	20·91	35·84	20 61	60·53	20·24	
52 26	22·37	25·37	31·22	49·05	17·23	
62·86	25·95	11·19	41·80	49·87	8·33	
72·90	27·10	...	...			

extensively by Perman and Saunders (*J. Chem. Soc.*, 1923, **123**, 841), Janecke (*Z. angew. Chem.*, 1928, **41**, 916), Janecke, Hamacher and Rahlfs (*Z. anorg. Chem.* 1932, **206**, 357) and lastly by Glass, Laybourn and Magdin (*J. Chem. Soc.*, 1933, 199) who have deduced the form of this binary system NH₄NO₃, KNO₃ and Pb(NO₃)₂ and have concluded that the two salts are isomorphous, capable of forming mixed crystals and that there is no evidence that pure ammonium nitrate separates from mixtures, rich in this salt. Our results are in agreement with their conclusions and it is quite evident that the results obtained by Bahl and Surjit Singh (*loc. cit.*) are erroneous.
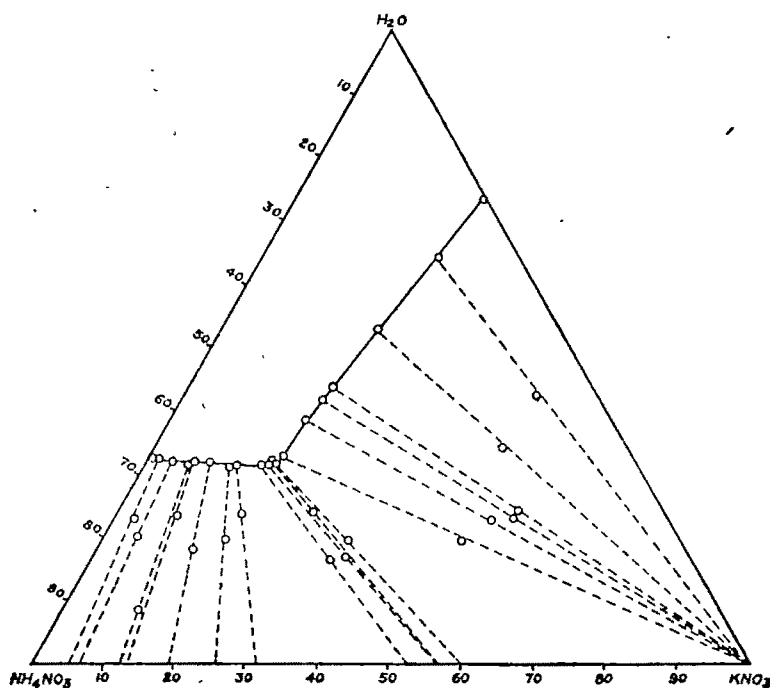
FIG. 1

Thanks are due to Dr. S. D. Muzaffar for guidance and keen interest he has taken in the work.

STUDIES IN SULPHANILAMIDES. PART I.
N¹-THIOBIAZOLYL-SULPHANILAMIDES

By P. C. GUHA AND D. B. DAS-GUPTA

Some N-thiobiazolyl sulphonate amides have been prepared with a view to testing their efficacy against bacterial infection.

Ever since the epoc-making discovery of the specific antistreptoccal action of Prontosil (hydrochloride of 4-sulphamido-2′ : 4′-diaminoazobenzene) by Domagk (*Deut. Med. Wschr.*, 1935, **61** 250; *Z. angew. Chem.*, 1935, **48**, 657; *Klin. Wschr.*, 1936, **15**, 1585) and of the simpler compound, sulphanilamide (*cf.* Trefouel *et al.*, *Compt. rend. Soc. Biol.*, 1935, **120**, 756; *Ann. Inst. Pasteur*, 1937, **58**, 30; Fuller, *Lancet*, 1937, **1**, 194), numerous compounds of this group have been prepared for testing their anti-bacterial property. It is, however, to be observed that out of these, only a few, *viz.*, sulphanilamide (I, R=H), sulphapyridine (II), sulphathiazole (III), sulphadiazine (IV) and sulphaguanidine (V), appear to find great favour in the treatment of the various bacterial infections at the present day.
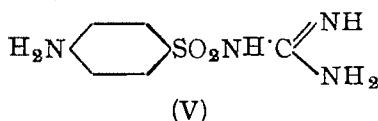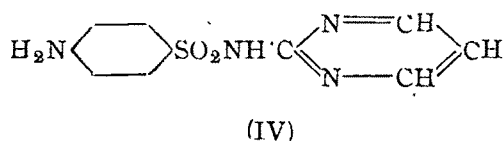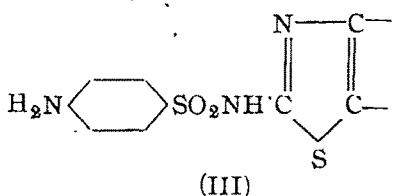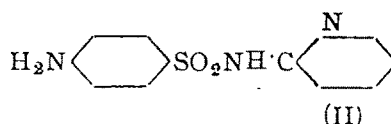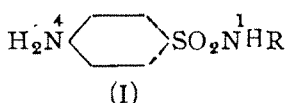
A close study of sulphonamides, hitherto described in literature, reveals the very interesting fact that majority of them that are found promising, possesses characteristic heterocyclic residues at N¹ (for nomenclature, *vide*, Crossley *et al.*, *J. Amer. Chem. Soc.*, 1938, **60**, 2217) and in a search for better drugs during the past three years, sulphonamide derivatives of pyridine, thiazole, diazine, pyrazine, piperazine, pyrole, thiophene, furane, acridine, quinoline, *iso*quinoline, carbazole, benzothiazole, etc., have been synthesised by various workers in the field and their pharmacological activity studied though without much success.

It has been the intention of the senior author (P.C.G.) ever since the inception of research on sulphonamides in this department; to study sulphanilamide derivatives possessing at N¹ various types of heterocyclic ring systems and open chain systems containing sulphur and nitrogen. The present paper forms the first part of a systema-

matic study of these compounds, and the preparation of sulphanilamide derivatives of 1:3:4-thiobiazole of the types (VI and VII) of 5-methyl-thiobiazole (VIII) and of 5-methyl-thiol-thiobiazole (IX) have been described. It may be observed in this connection that all

(VI)   (VII)   (VIII)   (IX)

where $R = H_2N\langle\quad\rangle SO_2-$
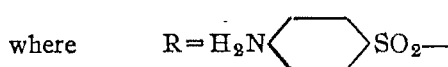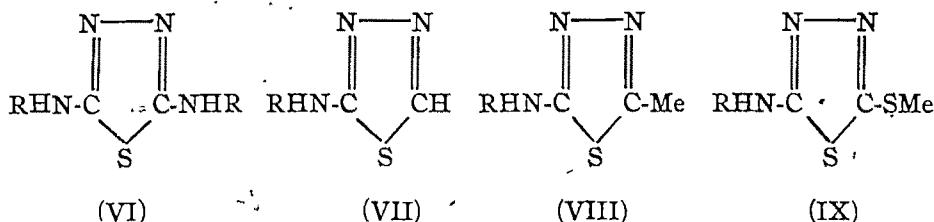
the compounds described in this paper contain the active grouping, $RNH \cdot C(:N-)-S-$ which is also present in the sulphathiazole molecule and it was thus expected that they would possess antibacterial properties.

EXPERIMENTAL

2 : 5-Di(acetylsulphanilamido)-1 : 3 : 4-thiobiazole (VI, $R = Ac \cdot NH \cdot C_6H_4SO_2-$).—A solution of 2 : 5-diamino-1 : 3 : 4-thiobiazole (5 g.), prepared according to Guha (*J. Amer. Chem. Soc.*, 1923, **45**, 1039), in acetone (40 c.c.) and pyridine (5 c.c.), was treated with crystallised *p*-acetylaminobenzene sulphochloride (18 g.), and heated on the water-bath for 2 hours. The solid separating, on cooling the solution, was filtered and crystallised from glacial acetic acid, m.p. 252-54°. (Found : N, 16·0; S, 18·2. $C_{18}H_{18}O_6N_6S_3$. requires N, 16·47 ; S, 18·82 per cent).

2 : 5-Di-(sulphanilamido)-1 : 3 : 4-thiobiazole (VI, $R = H_2N.C_6H_4SO_2-$).—The above acetyl compound (5 g.) was refluxed with 3N-hydrochloric acid (30 c.c.) for 3 hours. The hydrochloride obtained after evaporation of the product, gave on neutralisation with sodium carbonate, the free base which was crystallised from alcohol, m.p. 223°. (Found : N, 19·2; S, 21·8. $C_{14}H_{14}O_4N_6S_3$ requires N, 19·72 ; S, 22·53 per cent).

2-Sulphanilamido-1 : 3 : 4-thiobiazole (VII, $R = H_2N \cdot C_6H_4SO_2-$).—A solution of 2-amino-1 : 3 : 4-thiobiazole (5 g. Freund and Menicke, *Ber.*, 1896, **29**, 2514) in pyridine (25 c.c.) and acetone (10 c.c.) was treated with *p*-acetylaminobenzene sulphochloride (11·5 g.) and heated on the water-bath for 1 hour. After keeping the product overnight and dilution with water, a high melting substance was obtained. (Found : N, 17·9; S, 20·9. $C_{10}H_{10}O_3N_4S_2$ requires N, 18·79 ; S, 21·47 per cent) which was directly hydrolysed by boiling with 3N-hydrochloric acid (35 c.c.) till a clear solution was produced (about 2 hours.). After cooling and neutralising with sodium carbonate the sulphamido-thiobiazole separated. On crystallisation from alcohol it melted at 213-14°. (Found: N, 21·2; S, 24·7. $C_8H_8O_3N_4S_2$ requires N, 21·87 ; S, 25·0 per cent).

2-Acetylsulphanilamido-5-methyl-1 : 3 : 4-thiobiazole (VIII, $R = Ac.NH \cdot C_6H_4SO_2-$)— A solution of 2-amino-5-methyl-1 : 3 : 4-thiobiazole (5 g.) prepared according to the method of Freund and Menicke (*loc. cit.*) in pyridine (15 c.c.) and acetone (10 c.c.) was treated with *p*-acetaminobenzene sulphochloride (10 g.) and heated on the water-bath

for 2 hours. After keeping for 12 hours at room temperature the product, isolated in the usual way, crystallised from acetone, m.p. 220° (decomp.). (Found: N, 17·4; S, 20·0. $C_{11}H_{12}O_3N_4S_2$ requires N, 17·95; S, 20·51 per cent).

2-Sulphanilamido-5-methyl-1 : 3 : 4-*thiobiazole* (VIII, $R = H_2N \cdot C_6H_4SO_2$-) —The acetyl compound (5 g.) was boiled with 3N-hydrochloric acid (30 c.c.) for 3 hours when a clear solution was obtained. The solution was filtered, neutralised with sodium carbonate and the precipitated solid crystallised successively from alcohol and acetone, m.p. 186°-87°. (Found: N, 20·4; S, 23·2. $C_9H_{10}O_2N_4S_2$ requires N, 20·74; S, 23·7 per cent).

2-Acetylsulphanilamido-5-methylthiol-1 : 3 : 4-*thiobiazole* (IX, R = AcHN·C_6H_4SO_2-).— A solution of 2-amino-5-methylthiol-1 : 3 : 4-thiobiazole (5 g.), prepared essentially according to the method of Busch (*J. prakt. Chem.*, 1916, *ii*, **93**, 357), in alcohol (15 c.c.) and pyridine (20 c.c.) was treated with *p*-acetaminobenzene sulphochloride (8 g.) and heated on the water-bath for 1½ hours. The solid, that separated out on cooling, was crystallised from benzene, m.p. 216°-18°. (Found: N, 15·9; S, 27·2. $C_{11}H_{12}O_3N_4S_3$ requires N, 16·28; S, 27·9 per cent).

2-Sulphamido-5-methylthiol-1 : 3 : 4-*thiobiazole* (IX, R = H_2N·C_6H_4SO_2-).—The above acetyl compound (5 g.) was boiled with 3N-hydrochloric acid (28 c.c.) till a clear solution was obtained. After neutralisation of the product with sodium carbonate solution, the precipitated solid was collected and crystallised from hot alcohol, m.p. 198°. (Found: N, 18·2; S, 31·4. $C_9H_{10}O_2N_4S_3$ requires N, 18·54; S, 31·79 per cent).

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STUDIES IN SULPHANILAMIDES. PART II.
SYNTHESIS OF SULPHANILAMIDE COMPOUNDS POSSESSING SELENO-HETEROCYLIC RINGS

By A. N. Roy and P. C. Guha

Some sulphanilyl-2-aminoselenazoles and sulphanilyl-selenohydantoins have been synthesised for testing their potency against some experimental bacterial infections.

Ever since the discovery of the remarkable curative action of sulpha-pyridine in pneumococcal infections, the number of new sulphanilamide derivatives having hetero-cyclic residues at N^1 are on the increase and these include derivatives of pyridine, quinoline, acridine, thiazole, diazine, etc. It has, however, been established that out of the various hetero-sulphonamides only a few, e.g., sulphathiazole and sulphadiazine have actually been found to be very promising. It appears to be rather surprising that this line of research has not been extended to include heterocyclic systems containing elements other than nitrogen and sulphur in the rings. Selenium, the congener of sulphur in the periodic system, is known to possess very powerful antibactericidal properties but due to its pronounced and acute toxicity, its use in medicine is very limited. However, from time to time, patents have been taken on the preparation of organic selenium compounds and it has been claimed that the compound $C_6H_5 \cdot NH \cdot NH \text{-}p\text{-}C_6H_4\text{-}Se\text{-}C_6H_4\text{-}p\text{-}NH_2 \cdot C_6H_5 \cdot SO_3H$, prepared by the action of selenic acid on benzene-sulphanilamide, are endowed with highly efficient therapeutic properties [cf. U.S. Patent, Sept., 2,091,573, 1937]. It thus occurred to us worth while to undertake a thorough and systematic investigation on sulphanilamide compounds embracing cyclic ring systems of Se, Hg, As, etc., which are well known to possess therapeutic values

In the present paper, some sulphanilamide derivatives (preliminary note published in the *Proc. Indian Sci. Cong.*, 1941, p. 89,) containing selenazole (I) and selenohydantoin (II) residues at N^1, have been studied in view of growing interest of
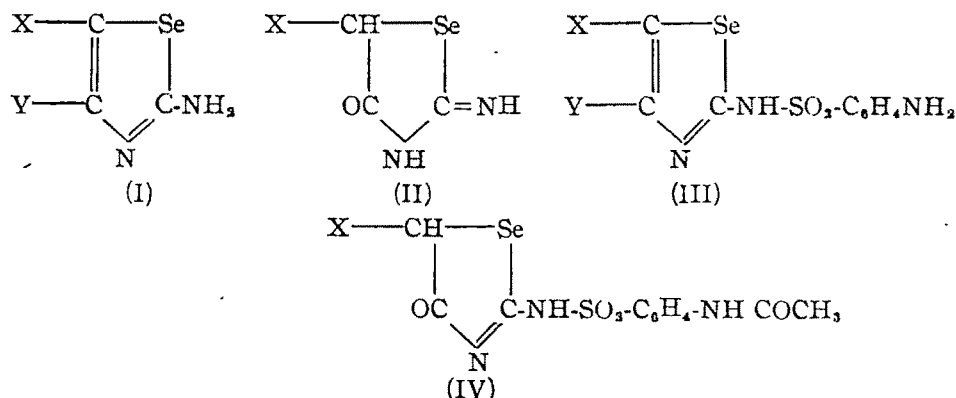
where X and Y = H, CH_3, C_6H_5, COOH, etc.

organo-selenium compounds in general (cf. *J. Indian Chem. Soc.*, 1941, **28**, 1) and the chemical resemblance of the above compounds with sulphathiazole in particular.

These compounds (I, II and III) have been prepared by following the older methods in general with only a few modifications. Thus in one case instead of the free base (II) its hydrochloride was employed due to its extreme instability under conditions

suitable for condensation with p-acetaminobenzenesulphonyl chloride. For the preparation of the required bases the method of Hoffmann (*Annalen*, 1889, **250**, 304) was adopted with modifications which invariably effected a definite improvement of the older process.

The pharmacological examination of these compounds will be reported in due course.

E x p e r i m e n t a l

2-Amino-4-methylselenazole was conveniently obtained by the following modification of Hoffmann's method (*loc. cit.*).

To a solution of freshly distilled chloroacetone (9·2 g.) in absolute alcohol (30 c.c.) powdered selenourea (6·1 g.) was stirred in with good shaking. The reaction started in the cold with gradual evolution of heat and was completed by heating on the water-bath for about 2 hours. The product was then cooled, basified with strong alkali and extracted with ether. The ether extract after drying over potassium carbonate and evaporation gave a residue (9·4 g.) which crystallised from benzene-petrol mixture (charcoal) in shining yellow needles, m.p. 78-79°.

2-(p-Acetaminobenzenesulphonyl)-amino-4-methylselenazole.—Freshly crystallised p-acetaminobenzene-sulphonyl chloride (8·8 g.) was slowly added to a solution of 2-amino-4-methylselenazole (6 g.) in pyridine (20 c.c.) with stirring. The reaction started in the cold with evolution of heat and was finally completed by heating on a water-bath for 2 hours. The reaction product was cooled, diluted with water and made slightly alkaline with ammonia, whereby the selenazole derivative separated. The compound was first purified by dissolving in dilute sodium hydroxide solution and precipitating out with dilute acetic acid. It was then repeatedly crystallised from alcohol (charcoal), m.p. 228-29°. (Found: N, 11·68. $C_{12}H_{13}O_3N_3SSe$ requires N, 11·72 per cent).

2-(p-Aminobenzenesulphonyl)-amino-4-methylselenazole.—The amine of the above acetyl compound may be obtained by both acid and alkali hydrolysis.

2-(p-Acetaminobenzenesulphonyl)-amino-4-methylselenazole (3 g.) was heated with 15% hydrochloric acid solution (20 c.c.) under reflux for ½-hour, whereby a clear solution was obtained. The amine was isolated by neutralising the mineral acid. It was well washed with benzene and crystallised from hot alcohol (charcoal), m.p. 222-23°. (Found: N, 13·2. $C_{10}H_{11}O_2N_3SSe$ requires N, 13·28 per cent).

2-Amino-4-phenylselenazole was best obtained by working up as follows :

Selenourea (6·1 g.) was stirred into a cold solution of freshly prepared ω-bromoacetophenone (9·9 g.) in alcohol (30 c.c.), which was then refluxed for one hour on the water-bath. On cooling, the solution deposited fine crystals of the hydrobromide of the base which were collected and decomposed with requisite amount of potash. The free base crystallised from hot benzene-petrol mixture as yellowish needles, m.p. 132-33°, yield 6·7 g.

2-(p-Acetaminobenzenesulphonyl)-amino-4-phenylselenazole.—The above base was converted into its acetylaminobenzenesulphonyl derivative in the usual manner in pyridine solution. The condensation, however, required heating for 5 to 6 hours at 100°. The crude acetyl compound was partly purified by dissolving in ammonia and precipitating with acetic acid. On crystallisation from hot alcohol after treatment with charcoal, it melted at 238-39°. It is insoluble in all the usual solvents. (Found: N, 9·88. $C_{17}H_{15}O_3N_3SSe$ requires N, 9·99 per cent).

2-(p-*Aminobenzenesulphonyl*)-*amino-4-phenylselenazole*.—The above acetyl compound was best hydrolysed with 5% alcoholic potash by refluxing for 4 hours. After removal of the solvent the product was acidified with acetic acid and the liberated amine, after reprecipitation from hydrochloric acid solutions by ammonia and a crystallisation from hot alcohol melts at 231-32°. (Found: N, 10·95. $C_{15}H_{13}O_2N_2SSe$ requires N, 11·10 per cent).

2-*Amino-4-methyl-5-carboxyselenazole*.—Ethyl α-chloroacetoacetate (16·6 g.), dissolved in absolute alcohol (30 c.c.), and selenourea (12·2 g.) were gradually mixed together and after the initial reaction had subsided the mixture was refluxed on the water-bath for 3 hours. On partial evaporation of alcohol under suction the hydrochloride of the base crystallised out on cooling. The free base, obtained by decomposing the salt with potash, crystallised from alcohol, as fine crystals containing two molecules of water of crystallisa-tion (*cf.* Hoffmann, *loc. cit.*). The anhydrous base melts at 181-82° (Hoffmann gives m p. 195°, decomp.). (Found: N, 13·55. $C_5H_6O_2N_2Se$ requires N, 13·64 per cent).

2-(p-*Acetaminobenzenesulphonyl*)-*amino -4- methylselenazole- 5- carboxylic Acid*.— The above amino acid was converted into its acetyl-sulphanilyl derivative by the usual manner by heating its pyridine solution for 3 hours at 100°. The crude product was well washed with dilute hydrochloric acid (10%), with water and with benzene (after drying). After repeated crystallisation from alcohol, the acetyl compound separated with two molecules of water of crystallisation. After drying at 120° for several hours the anhydrous compound melted at 238-39°. (Found: N, 10·37. $C_{13}H_{13}O_5N_3SSe$ requires N, 10·44 per cent).

2-(p-*Aminobenzenesulphonyl*)- *amino -4- methylselenazole -5- carboxylic Acid*.—The above acetyl compound was hydrolysed by refluxing with hydrochloric acid (18%) for ½ hour, alcohol being added to effect a complete solution. After neutralising the product with ammonia, the separated base, m.p. 231-32°, was collected and crystallised from alcohol (charcoal). (Found: N, 11·57. $C_{11}H_{11}O_4N_3SSe$ requires N, 11·66 per cent).

Selenohydantoin.—Monochloroacetic acid (9·5 g.), dissolved in absolute alcohol (25 c.c.), was condensed with selenourea (12·3 g.) by refluxing on the water-bath for 2 hours. On cooling the solution deposited shining needles of the hydrochloride of the base. As the free base (m.p. 190°, decomp.), obtained by treatment of the salt with potash, did not keep well in air, the hydrochloride was directly used for further experiments.

2-(p-*Acetylaminobenzenesulphonyl*)-*aminoselenohydantoin*.—To a mixture of selenohydantoin hydrochloride (6 g.) and *p*-acetaminobenzene sulphochloride (7·5 g.), pyridine (25 c.c.) was gradually added and the product was heated at 105-110° for 2 hours out of contact with air. Working up in the usual way, a red solid product was obtained which crystallised from hot alcohol (charcoal), m.p. 263-64° (decomp.). (Found: N, 11·71. $C_{11}H_{11}O_4N_5SSe$ requires N, 11·66 per cent). The substance is practically insoluble in all the usual organic solvents except hot alcohol in which it is only sparingly soluble.

SYNTHESIS OF *TRANS-ANTI-TRANS*-9-KETO-PERHYDRO-PHENANTHRENE*

By BIDYUT KAMAL BHATTACHARYYA

A general method has been described for the synthesis of perhydrophenanthrene.

With the elucidation of the structures of sterols and bile acids, the chemistry of perhydrophenathrene has gained singular importance. Recently Linstead *et al* (*J. Chem. Soc.*, 1939, 842, 850; *J. Amer Chem. Soc.*, 1942, 64, 1991) have initiated a thorough investigation of the stereochemical problem that arises out of the four asymmetric carbon atoms in the perhydrophenanthrene molecule and in this connection they have prepared all the possible stereochemically homogeneous perhydrodiphenic acids and have used them as reference compounds for the determination of configurations of different perhydrophenanthrenes. For the preparation of the three stereochemically homogeneous perhydrophenanthrene derivatives, whose configurations have been settled, the above authors have employed the method of catalytic hydrogenation of aromatic and partially aromatic phenanthrenes and also that of 9-keto-$\Delta^{10 \cdot 11}$-dodecahydrophenanthrene obtained by the method of Rapson and Robinson (*J. Chem. Soc.*, 1935, 1285). It is interesting to note that the 9-keto-perhydrophenanthrene, obtained by the last method, has been shown, by its oxidation to one of the diphenic acids, to possess the *trans- anti-trans* configuration which is identical with the configuraion assigned to the rings A, B, and C of the cholestane system occurring in nature. The above methods, however, have so far not found their application for the preparation of the perhydrophenanthrene derivatives with the angular methyl groups.

Quite recently, Robinson *et al* (*J. Chem. Soc.*, 1941, 386; 1943, 491) have succeeded in synthesising 9-keto-$\Delta^{8 \cdot 14}$-13-methyl-dodecahydrophenanthrene and an isomer of androsteredione. But the method of Manich's base condensation (DuFeu, McQuillin and Robinson, *J. Chem. Soc.*, 1937, 53), which has been utilised for the preparation of the above substances, generally gives rise to the *cis* configuration of the fused carbon rings (Linstead, Millidge and Walpole, *J. Chem. Soc.*, 1937, 1140).

The present paper describes a method for the building up of perhydrophenanthrene nucleus which offers the possibility of application in the synthesis of *cyclo*pentanoperhydrophenanthrene with angular methyl groups.

For the preparation of 2-(2'-carbethoxy-*cyclo*hexyl)-*cyclo*hexanone derivatives which have been utilised as the starting materials a method similar to that of Banerjee (*J. Indian Chem. Soc.*, 1940, 27, 453) and Banerjee and Roy (*Science & Culture*, 1944-1945, 10, 134) has been successfully employed. Attempts to prepare the same starting material by the Michael condensation between ethyl *cyclo*hex-1-ene-2-carboxylate and *cyclo*hexanone, or ethyl *cyclo*hexanone-2-carboxylate (Rapson, *J. Chem. Soc.*, 1936, 1626) proved to be futile. Ethyl *cyclo*hex-1-ene-2-carboxylate, prepared from *cyclo*-

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hexanone cyanohydrin in the usual way, has been allowed to react with ethyl sodiocyano-acetate. The potassio derivative of (I) is condensed with ethyl 5-iodovalerate (Banerjee and Roy, *loc. cit.*) to yield(II, R=CN). The optimum yield is obtained when the temperature of the reaction mixture is allowed to rise to the boiling point in course of several hours (*cf.* Mitter and Bhattacharyya, *J. Indian Chem. Soc.*, 1942, **19**, 69). The condensation product is hydrolysed and esterified to furnish (II, R=H) which on treatment with sodium dust gives (III, R=CO_2Et). The Dieckmann product gives positive ferric reaction and can not be distilled without decomposition. It is hydrolysed and esterified to yield (III, R=H) which is reacted with activated zinc and ethyl bromoacetate. The hydroxy diester (IV, R=OH ; $R_1=R_2=C_2H_5$) is dehydrated in ethereal solution with thionyl chloride and pyridine to the corresponding unsaturated ester (V, R=C_2H_5) which on hydrolysis furnishes a solid dicarboxylic acid (V, R=H). The unsaturated acid on hydrogenation yields a solid saturated dicarboxylic acid (IV, R=$R_1=R_2=$H) which is esterified with diazomethane. The diester (IV, R=H ; $R_1=R_2=CH_3$), thus obtained, has been cyclised to yield 9-keto-10-carbomethoxy-perhydrophenanthrene in excellent yield. 9-Keto-perhydrophenanthrene (VI) is obtained in the liquid state by hydrolysis of the above β-ketonic ester in the usual manner. The above ketone has been converted into its oxime and after several crystallisation from ethanol melts at 226-27° (lit. 227-28°; Linstead and Walpole, *J. Chem. Soc.*, 1939, 842). The ketone is regenerated from its oxime and after purification by distillation solidifies, m.p. 46-47·5° (lit. 49°; Linstead and Walpole, *loc. cit.*). A portion of the above liquid ketone (VII) is oxidised with a mixture of concentrated and fuming nitric acids to furnish a perhydrodiphenic acid, m.p. 240-41° (lit. 237-40° and 246-47°, Linstead and Doering, *J. Amer. Chem. Soc.*, 1942, **64**, 1991 ; 243-44°, Linstead and Walpole, *J. Chem. Soc.*, 1939, 850).

The above experimental evidences show that the synthetical 9-keto-perhydrophenanthrene obtained by the method detailed above possesses *trans-anti-trans* stereochemical configuration represented by (VI). Here the stereochemical configuration of the four asymmetric carbon atoms C_{11}, C_{12}, C_{13} add C_{14} in the synthetical specimen is also identical with that of cholane system occurring in nature.

(VI)
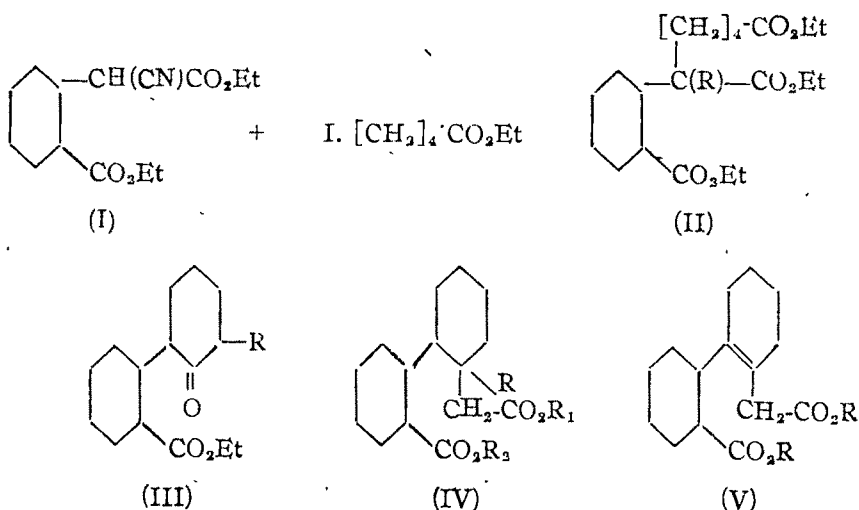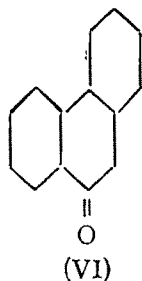
EXPERIMENTAL

*cyclo*Hexanone cyanohydrin was prepared according to the method of Clemo and Welch (*J. Chem. Soc.*, 1928, 2629). When the temperature of the reaction mixture was maintained between 2° and 5° by external cooling the yield was quantitative.

Ethyl cyclohex-1-ene-2-carboxylate.—The above cyanohydrin (210 g.) in pyridine (272 g.) was cooled in a freezing mixture and dehydrated with thionyl chloride (130 c.c.). The reaction product was worked up in the usual way, yield 167 g.

The unsaturated nitrile was hydrolysed with aqueous caustic potash according to the method of Linstead and Boorman (*J. Chem. Soc.*, 1933, 258).

The unsaturated acid (12·7 g.) was esterified by refluxing with alcohol (50 c.c.) and sulphuric acid (5 c.c., d, 1·84) for 24 hours, yield 13·5 g. The ester could be directly obtained from the nitrile (13·6 g.) by refluxing with a mixture of rectified spirit (25 c.c.) and concentrated sulphuric acid (4·3 c.c.) for 36 hours, yield 13 g.

*Ethyl 2-carbethoxy-*cyclohexyl-1-cyanoacetate (I).—A mixture of the above unsaturated ester (181 g.) and ethyl cyanoacetate (168 c.c.) was added to sodium ethoxide (prepared from 30·2 g. of sodium) in alcohol (370 c.c.). The reaction mixture was heated on the water-bath for 30 hours, diluted with iced dilute hydrochloric acid and extracted with ether. The ethereal layer was washed with sodium bicarbonate solution, dried and distilled, yield 228 g.

Ethyl 5-Bromovalerate.—Allyl iodide was prepared according to Dutta (*J. Amer. Chem. Soc.*, 1914, **36**, 1005).

(a) Allyl iodide (34 g.) was added to magnesio malonic ester (Mg. 2.4 g. ; malonic ester, 32 g. ; alcohol, 34 c. c. and carbon tetrachloride, 1 c.c.) and the reaction mixture was refluxed for 12 hours and worked up as usual, yield 18 g. (Lund, *Ber.*, 1934, **67**, 935).

(b) Allyl iodide (40 g.) was added to sodiomalonic ester (prepared from sodium 5.5 g. ; malonic ester, 56 c.c. and alcohol, 55 c.c.) and the reaction mixture was refluxed for 12 hours. The yield was quantitative. The use of benzene as solvent in the above condensation furnished a quantitative yield of the product.

5-Bromovaleric acid (50 g.), obtained from allyl malonate, following the method of Linstead (*J. Chem. Soc.*, 1933, 575) was esterified with alcohol (150 c.c.) and sulphuric acid (9 c.c.) by refluxing for 24 hours, yield 50 g.

*Diethyl 2-Cyano-2 (2'-carbethoxy-*cyclohexyl)-*pimelate.*—Ethyl 5-iodovalerate (56 g.) was added to the potassio derivative of the above cyanoacetic ester (I), prepared from

potassium (9 g.), cyanoester (70 g.) and xylene (150 c.c.). The reaction mixture was left overnight, heated on the water-bath for 12 hours, at 110° for another 12 hours and finally refluxed in an oil-bath for 12 hours. It was washed thrice with water, dried and distilled, b. p. 179-82°/0·4 mm., yield 56 g.

The use of bromo ester in the above condensation also yielded the final product (56 g.). But the use of a mixture of xylene and alcohol as solvent furnished a rather poorer yield of the final product. (Found : C, 63·9 ; H,. 8·5. $C_{21}H_{33}O_6N$ requires C, 63·79 ; H, 8·35 per cent).

Diethyl 2-(2'-carbethoxy-cyclohexyl)-pimelate.—The above substituted cyano ester (56 g.) was hydrolysed by refluxing with a mixture of glacial acetic acid (140 c.c.) and concentrated sulphuric acid (100 c.c.) and water (140 c.c.) for 36 hours. It was next diluted with water and the precipitated acid was extracted with ether. The crude acid was esterified with alcohol (206 c.c.) and sulphuric acid (28 c.c.) by refluxing for 40 hours. The ester was worked up and distilled, b. p. 190°/4 mm., yield 42 g. (Found : C, 66·98 ; H, 9·44. $C_{20}H_{34}O_6$ requires C, 64·87 ; H, 9·18 per cent).

2-(2'-Carbethoxy-cyclohexyl)-cyclohexanone.—The above pimelate (33 g.) was refluxed with sodium dust (4 g.) in benzene (160 c.c) until the whole of sodium had reacted. The reaction mixture was decomposed with iced dilute sulphuric acid and the precipitated β-ketonic ester was extracted with ether and washed with sodium bicarbonate solution. The ether-benzene layer was dried and distilled, but the β-ketonic ester could not be distilled without decomposition. The alkaline washing was acidified and the precipitated oil after extraction with ether was mixed with the neutral β-ketonic ester. The β-ketonic ester gave a violet colouration with alcoholic ferric chloride. The crude product was hydrolysed by refluxing it with a mixture of glacial acetic acid (20 c.c.) and concentrated hydrochloric acid (100 c.c.) and water (10 c.c.) for 30 hours. The acid together with water were removed under reduced pressure and the residue, thus obtained, was esterified with alcohol (100 c.c.) and sulphuric acid (10 c.c.) by refluxing for 24 hours. The resulting ester was worked up and distilled, b. p. 151°/4·5 mm. (Found : C, 71·3 ; H, 9·42. $C_{15}H_{24}O_3$ requires C, 71·42 ; H, 9·52 per cent).

The oxime was prepared by refluxing the keto-ester (0·5 g.) with an excess of hydroxylamine hydrochloride, pyridine and alcohol. It was obtained in silky needles, m.p. 138-40°. (Found : C, 67·72 ; H, 9·44. $C_{15}H_{25}O_3N$ requires C, 67·41 ; H, 9·4 per cent).

Attempts for the preparation of (III, R=H).—(a) A solution of ethyl *cyclo*hex-1-ene-2-carboxylate (16 g.) in alcohol (16 c.c.) was added to a solution of potassium ethoxide (potassium 1 g., ether 10 c.c , and alcohol 33 c.c.) cooled in freezing mixture and then it was left for several days. No reaction took place.

(b) A mixture of ethyl potassio *cyclo*hexanone-2-carboxylate (metal. 3·9 g., β-keto-ester, 17 g.) in alcohol (20 c.c.) and pyridine (20 c.c.) and *cyclo*hex-1-ene-2-carboxylate (10·7 g.) was refluxed for 40 hours. But no reaction took place.

(c) A solution of ethyl *cyclo*hex-1-ene-2-carboxylate (15·8 g.) in ether (30 c.c.) was added to a boilling ethereal mixture of sodio*cyclo*hexanone prepared from sodamide (4 g.), *cyclo*hexanone (9·8 g.) and ether (150 c.c.). It was refluxed for 8 hours and on working up as usual no product could be isolated.

Ethyl (2'-carbethoxy-cyclohexyl)-cyclohex-1-ene-2-acetate.—The above keto-ester

(III, R = H, 17 g.) was refluxed with a mixture of thiophene-free benzene (150 c.c.), zinc (5 g.), ethyl bromoacetate (8 c.c.) and a crystal of iodine for 2 hours. Next a lot of zinc (2 g.), a crystal of iodine and ethyl bromoacetate (4 c.c.) were added and the mixture refluxed for 1 hour. Another lot of zinc (2 g.) and a crystal of iodine were added and the heating continued for another 2 hours. The product was decomposed with iced dilute sulphuric acid, extracted with benzene, washed with dilute ammonia and water, b. p. 140-50°/0.4 mm.

The above hydroxy compound in a mixture of ether (100 c.c.) and pyrdine (20 c.c.) was dehydrated with thionyl chloride (10 c.c.). The reaction mixture was left overnight and decomposed with iced dilute acid and worked up in the usual way, b. p. 180°/4 mm., yield 5.8 g. (Found : C, 70.72 ; H, 9.22. $C_{19}H_{30}O_4$ requires C, 70.8 ; H, 9.31 per cent).

1-(2'-*Carboxy*-cyclohexyl)-cyclohex-1-ene-2-acetic *Acid.*—The above unsaturated compound (5 g.) was hydrolysed by refluxing it with methanolic caustic potash (5 g. in 50 c.c.) for 2 hours and then for another 7 hours with aqueous potash (5 g. in 5 c.c.). The methanol was removed and the dilute solution was extracted with ether. The alkaline solution was acidified with acetic acid and then extracted with ether. After removal of ether the residue was boiled with acetic acid, charcoaled and filtered. The unsaturated dibasic acid was next crystallised from methanol. It began to melt with decomposition at 195°, almost clear at 200° and perfectly clear at 205°, yield 3 g. (Found : C, 68.00 ; H, 8.4. $C_{16}H_{22}O_4$ requires C, 67.67 ; H, 8.27 per cent).

2'-*Carboxyl-dicyclohexyl-2-acetic Acid.*—The above unsaturated acid (2.8 g.) was hydrogenated in acetic acid solution over Adam's catalyst (0.3 g.). It was crystallised from benzene, m. p. 188-89°. (Found : C, 67.45 ; H, 9.15. $C_{16}H_{24}O_4$ requires C, 67.16 ; H, 8.95 per cent).

Methyl 2'-carbomethoxyl-dicyclohexyl-2-acetate—An ethereal solution of diazomethane was added to the above acid (2.8 g.) in ether (200 c.c.). The reaction mixture was allowed to stand for 2 days. The excess of diazomethane was destroyed with acetic acid. and the ethereal layer was washed with sodium bicarbonate solution, dried and distilled, b. p. 153°/3 mm., yield 2.8 g. (Found : C, 68.89 ; H, 9.35. $C_{17}H_{28}O_4$ requires C, 68.9 ; H, 9.45 per cent).

9-*Keto-perhydrophenanthrene.*—The above ester (2.8 g.) was refluxed with benzene (40 c.c.) and sodium dust (0.46 g.) for 6 hours when all the sodium went into solution. It was worked up as mentioned before. The β-keto-ester gave a light violet colouration with alcoholic ferric chloride and was hydrolysed, as mentioned before, and distilled, b. p. 133°/4.5 mm, yield 1.2 g.

A mixture of the above ketone (0.4 g.), hydroxylamine hydrochloride (0.6 g.), pyridine (1 c.c.) and alcohol (2.5 c.c.) was refluxed for 4 hours. After diluting the reaction mixture the oxime was crystallised from large amount of ethanol in milk-white silky needles, m. p. 226-27°. (Found : C, 76.2 ; H, 10.48. $C_{14}H_{23}ON$ requires C, 76.01 ; H, 10.4 per cent).

The above oxime (0.25 g.) was refluxed with 5% sulphuric acid (25 c.c.) for 6 hours. The solution was extracted with ether, washed with sodium bicarbonate solution and water, dried and distilled. The distillate solidified with an adhering oil which was removed on a porous plate, m.p. 46-47.5°.

5—1547P—6

Perhydrodiphenic-1:1'-dicarboxylic Acid.—The above 9-keto-perhydrophenanthrene (0·7 g.) was treated with a mixture of concentrated and fuming nitric acids (1:3 ; 3·2 c.c.) and the mixture was heated on the steam-bath for 45 minutes.   On cooling and diluting the reaction mixture with water a solid with some tar separated out.   It was thrice crystallised from dilute acetic acid in needles, m.p. 240-41°.   (Found : C, 66·36 ; H, 8·7. $C_{14}H_{22}O_4$ requires C, 66·19 ; H, 8·66 per cent).

It is a great pleasure to record my sincere thanks to Prof. Dr. P. C. Mitter for his valuable advice and encoragement and to Dr. D. K. Banerjee for his generous help during the course of this investigation.   My thanks are also due to Mr. N. Ghosh, M.Sc. for microanalysis of the compounds.

SYNTHESIS OF A TRIPHENYLSULPHANE SYSTEM

By J. D. Billimoria, A. N. Kothare and V. V. Nadkarny

Thionyl chloride reacts with dimethylaniline producing hexamethyl-triaminotriphenylsulphane. In the presence of an inert solvent tetramethyldiaminodiphenylsulphoxide is formed and the latter may be condensed with another molecule of dimethylaniline forming the dye, hexamethyl-triaminotriphenylsulphane.

Michaelis (*Annalen*, 1904, **274**, 173, 180) has reported that both aliphatic and aromatic primary amines react with thionyl chloride to yield thionyl amines,

$$3RNH_2 + SOCl_2 \longrightarrow R-N = SO + 2RNH_2, HCl$$

(where $R = $ alkyl or aryl group). The primary aryl amines give blue coloured compounds sparingly soluble in water, when the reaction is carried out in the absence of a solvent. The secondary amines on the other hand are known to react with thionyl chloride only in the presence of anhydrous aluminium chloride to give substituted diphenyl sulphoxides.

$$2C_6H_5NH \cdot CH_3 + SOCl_2 \xrightarrow{AlCl_3} (C_6H_4NHCH_3)_2 \cdot SO.$$
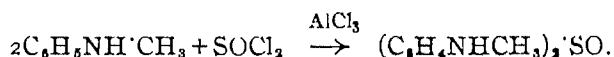
As there is no reference to the action of $SOCl_2$ on a tertiary amine, we took up the study of the reaction of thionyl chloride with dimethylaniline as a typical tertiary amine. The reaction has been carried out both in the presence of an inert solvent such as petroleum ether and in its absence. In the absence of the solvent thionyl chloride reacts with dimethylaniline at room temperature liberating dense greenish white fumes and producing a heavily coloured blue dye. The reaction has been next carried out at the temperature of ice, and the colour base of the dye is precipitated by ammonia, as faintly coloured and tarry in nature. It is dried in vacuum for over two weeks, then dissolved in chloroform and · converted into the hydrochloride by passing hydrochloric acid gas into the chloroform solution. The hydrochloride, so obtained, is also tarry and may be dried in vacuum to a blue powder that cannot be crystallised, m.p. 108-12°. All attempts at crystallising the dye as a double oxalate also failed.

· The formation of the dye may be formulated as follows :—

(I)   (II)
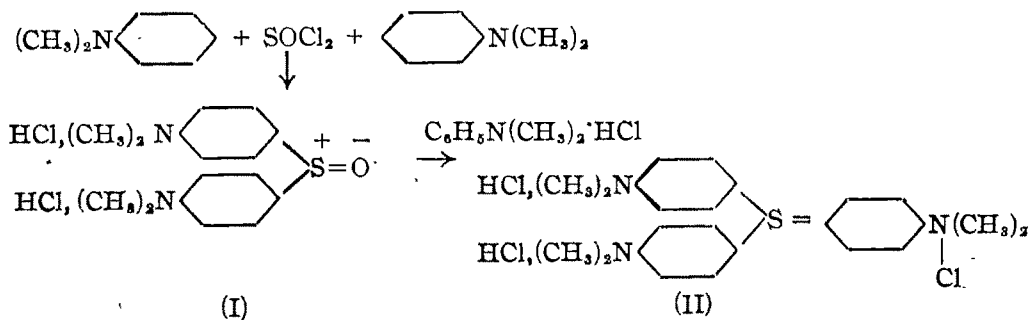
The conversion of (I) into (II) bears a close analogy to the conversion of Michler's ketone into malachite green.

The above proposed mechanism of the formation of the dye is based on the following evidence. Michaelis (*loc. cit.*) has reported the formation of sulphoxide derivatives by the interaction of thionyl chloride and monomethylaniline in the presence of aluminium chloride. As the *para* position of dimethylaniline is very active a similar condensation would take place in the case of this tertiary base giving the compound (I) even without the use of a condensing agent. Such a condensation product has actually been isolated by us by carrying out the reaction between thionyl chloride and dimethylaniline in the presence of an inert solvent like petroleum ether at the temperature of ice. The reddish yellow tarry product, first obtained after crystallisation from methyl alcohol, gives colourless cubes, m.p. 243-44°. The molecular weight as determined by the Rast's method is in agreement with the formula (I).

The sulphoxide (I), thus obtained, has been condensed further with one molecule of dimethylaniline in the presence of phosphorous oxychloride to give the dye (II).

The blue dye, thus obtained, is structurally similar to a triphenylmethane dye; in its observed properties it shows similarity to such dyestuffs. It is found to be a basic dye which dyes cotton, silk and artificial silk from a tannin-mordanted bath. Like basic dyes, it is not fast to sunlight when dyed on cotton. However, it is found to be much faster on artificial silk.

The dye forms lakes with aluminium and zinc salts; with the addition of zinc chloride. and alkali the lake is obtained in the form of a blue powder. The aluminium lake, when freshly prepared, is soluble in dilute hydrochloric acid but after standing for some days it is rendered insoluble. The zinc lake is soluble in dilute acids.

The chloride of the dye gives a pure shade of blue on cotton, and the acetate a violet-blue; with alkali an almost colourless dye base is precipitated which can be re-converted into the dye by the addition of acid.

EXPERIMENTAL

Hexamethyltriaminotriphenylsulphane.—To dimethylaniline (24·3 c.c.), placed in a round-bottomed flask and cooled to '–10°, was added thionyl chloride (10 c.c.) dropwise, with constant stirring, during a period of 1 hour. The reaction proceeded violently in the beginning but gradually subsided; after standing for 2 hours, a further quantity of dimethylaniline (20 c c.) was added to the reaction mixture and the whole heated on a water-bath for 6 hours in a current of dry hydrochloric acid gas.

The reaction mixture was then thrown into cold water (500 c.c.) when the impure dye was precipitated; it was dissolved in hot water and the dye base precipitated by the addition of sodium carbonate solution; the excess of the dimethylaniline was removed by steam-distillation. The dye base was then dissolved in hydrochloric acid, cooled by addition of ice and the dye precipitated by the addition of iced ammoniacal brine. The dye was then filtered off at the pump. It is a viscous tarry product which does not crystallise from any one of the common solvents. A solution in dry pyridine was allowed to evaporate slowly in a vacuum desiccator when at the end of two weeks, a dark blue powder was obtained, m.p. 108-12°. (Found: C, 56·1; H, 5·9; N, 7·62;

S, 5·60 ; M.W., 458. $C_{24}H_{32}N_3Cl_3S$ requires C, 57·6; H, 6·4; N, 8·4; S, 6·4 per cent. M.W., 500·5).

Tetramethyldiaminodiphenylsulphoxide.—An excess of thionyl chloride (6 c.c.), dissolved in petroleum ether (50 c.c.), was added in small portions at a time, during a period of half an hour to a solution of dimethylaniline (10 c.c.) in petroleum ether (100 c.c.), cooled to 0°. The hydrochloride of the sulphoxide was precipitated out as a tarry product. The petroleum was removed by distillation under reduced pressure ; the product, still a tarry one, was then freed from excess of thionyl chloride by shaking with petroleum ether. It was then dried in a vacuum desiccator for several days and finally crystallised from methyl alcohol with great difficulty in fine cubes, m.p. 243-44° ; yield 78%. (Found : N, 7·59 ; Cl, 19·2 ; S, 8·71 ; M. W. 353. $C_{16}H_{22}ON_2Cl_2S$ requires N, 7·76 ; Cl, 19·4; S, 8·86 per cent. M.W., 361.)

Condensation of the Sulphoxide with Dimethylaniline.—A solution of the sulphoxide (10 g.) in dimethylaniline (20 c.c.) was heated with phosphorus oxychloride (10 c.c.) on the water-bath for 2 hours.

The contents of the flask were poured into water (500 c.c.), rendered just alkaline with sodium carbonate and distilled in steam. The product, when free from dimethylaniline, was dissolved in hydrochloric acid cooled to 10° and the dye precipitated by the addition of ammoniacal brine. It was dissolved in dry pyridine and was allowed to crystallise and the tarry product dried in vacuum for several days, m.p. 110-14°, the m.p. with the dye originally obtained being depressed by 3-4°. (Found : C, 55·9 ; H, 6·0 ; N, 7·48 ; Cl, 20·5 ; S, 5·3. $C_{24}H_{32}N_3Cl_3S$ requires C, 57·60 ; H, 6·4 ; N, 8·4 ; Cl, 21·2 ; S, 6·4 per cent).

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A NOTE ON THE ESTIMATION OF ZINC

By S. SEN

The usual method of estimation of zinc is by its separation as ZnS, dissolving and precipitation as $Zn(NH_4)PO_4$ and weighing as $Zn(NH_4)PO_4$ after drying or as $Zn_2P_2O_7$ after ignition. This lengthy method can be easily replaced if a standard volumetirc method, free from the usual drawbacks, can be obtained. The following work was undertaken with a view to normalising the conditions of potassium ferrocyanide tritration with a suitable indicator.

For the titration of zinc with potassium ferrocyanide numerous indicators have been suggested, both external and internal, but owing to the necessity of carefully controlled conditions of experiment and also to the colour change being not very distinct, their use is limited. Along with indicators like $FeSO_4$, diphenylamine, uranium nitrate (*J. Amer. Chem. Soc.*, 1927, **49**, 356; *Chemist and Analyst*, 1928, **17**, 14; *Chem. Weekblad.*, **24**, 203), ammonium molybdate (Giorn, *Chem. Ind. Appl.*, 1924, **6**, 234) has been tried and found to be more suitable than others. As the actual experimental results could not be obtained, a detailed study of this indicator has been made.

Factors influencing the end-point in the above titration are : (i) acidity, (ii) temperature, and (iii) presence of ammonium salts.

In cold acid solution the end-point is variable, in strongly acid solution it is not at all detectable. To get a quick end-point, the solution should be kept moderately hot, near about 50 to 60°, and an acid concentration of 5% in the final volume should be maintained. Ammonium chloride also helps in getting a sharp end-point. If it is not present, premature end-point is obtained or otherwise the titration has to be carried out very slowly. The following procedure may be conveniently adopted.

EXPERIMENTAL

Dissolve the sample, containing 0·03 g. ZnO in 25 c.c. of HNO_3 or HCl as found convenient. After filtration and washing off the metals like Pb, Sn, Ni, Cu, etc., if any, neutralise with ammonia, using phenolphthalein as indicator, bring the volume to 100 c.c., add 5 c.c. of glacial acetic acid and 10 c.c. of 10% ammonium chloride. Add 0·5 c.c. of 2% of ammonium molybdate solution (aqueous) and titrate with potassium ferrocyanide solution to a chocolate brown end-point. If traces of iron be present, the colour change at the end-point is from azure blue to chocolate brown, but much iron gives variable end-point and should be avoided by removal.

It has been observed that the more dilute the zinc solution, the longer it takes for attaining the equilibrium.

TABLE I

Sample.	Gravimetric.	Volumetric.	Diff.	% Error.
Zinc oxide	80·18%	80·08%	0·10	−0·12
,, ,,	80·12	80·00	0·12	−0·14
,, ,,	80·20	80·11	0·09	−0·11
,, ,,	80·03	79·81	0·22	−0·26
Pigment	32·52	32·48	0·04	−0·12
,,	24·41	24·30	0·11	−0·45
Brass	40·16	40·00	0·16	−0·40
,,	39·80	39·72	0·08	−0·20

The following indicator has been tried with considerable success. The end-point is from blue to colourless. Although an outside indicator yet easy detection of the end-point makes it all the more convenient for use.

Preparation of the Indicator.—Take a 10% solution of ferric chloride, oxidise with a few drops of nitric acid. to ensure all the iron is in the oxidised condition, boil for 5 min., cool, discharge the yellow colour with dropwise addition of phosphoric acid (d, 1·75) and then 1 c.c. of HNO_4 in excess. A filter paper 'soaked with this solution is an external indicator.

Standardisation of $K_4Fe(CN)_6$ (34 g. per litre).—Take 50 c.c. of the solution, add 1 c.c. of HCl (1:1) and make up the volume to 100 c.c. Titrate with $N/50$-$KMnO_4$ until a drop of the solution no longer gives a blue colour. (A persistent blue ring, the inner zone being colourless, shows the presence of some unoxidised iron in the indicator). Repeat the titraton with an addition of 25 c.c. of zinc solution, (2 g. ZnO per 500 c.c.) after neutralising and acidifying in a similar way. The difference between the two titres gives the number of c.c. equivalent to the amount of Zn present in 25 c.c. of the ZnO solution.

Estimation.—Dissolve 0·2 to 0·3 g. of the sample in 25 c.c. HNO_3. Filter and wash and after adjusting the acid concentration to 15% and boiling to remove any nitrous fume, electrolyse with platinum electrodes (6 volts and 0·4 amp.) for an hour. Add 2g. of NH_4Cl, neutralise and precipitate Fe or any other third group metal. Filter and wash, add a few drops of methyl orange and carefully neutralise with HCl and add 1 c.c. in excess. The volume at this time should be near about 100 c.c. Titrate as above. The estimation should be done, as usual, after removal of Sn, Pb, Fe, Ni, and Cu.

TABLE II

Sample.	Gravimetric.	Volumetric	Diff.	% Error
Zinc oxide	80·18%	80·00%	0·18	0·22
,, ,,	80·12	80·10	0·10	0·02
,, ,,	80·20	80·11	0·09	0·11
,, ,,	80·03	80·13	0·10	0·12
Pigment	32·50	32·10	0·40	1·25
,,	24·41	24·09	0·32	1·33
,,	20·08	20·10	0 02	0·10
,,	15·56	15·50	0·06	0·38
,,	15·13	15·06	0·07	0·46
Brass	40·16	40·09	0·07	0·17
,,	39·80	39·60	0·20	0·50
,,	40·20	40 16	0·04	0·10
,,	38·86	38·81	0·05	0·12
,,	36·55	36·64	0·09	0·25
,,	41·11	41·09	0·02	0·05
Bronze	4·20	4·18	0·02	0·50
,,	4·16	4·14	0·02	0·50
Bearing metal	12·03	12·00	0·03	0·25
,, ,,	10·54	10·59	0·05	0·48

The above method is very suitable for the estimation of ZnO in pigments and also Zn in non-ferrous metals and the estimations have been done mainly on those two materials.

The authors express their indebtedness to the authorities of the Ordnance Laboratories for giving facilities to undertake the above works.

CHEMISTRY OF THE RARE-EARTHS. PART IV. BASIC NITRATES OF CERIUM EARTHS

By Nihar Kumar Dutt.

The basic nitrates of cerium earths have been studied and described. Thermometric and conducto-metric titration curves have shown the existence of two basic salts each, $RONO_3$ and R_2O_3, $2RONO_3$ respectively, both insoluble and having compositions similar to those for bismuth.

Though the differential decomposition of nitrates had been utilised for the isolation of yttrium earths since the classical work of Berlin (*Forhandl. Scand. Naturf. Kjoben-havin*, 1860, **8**, 448) no systematic study of the basic nitrates of rare earths has been made up till now.

By carefully heating the hydrated salts, basic nitrates are obtained, which in the yttrium group are soluble in water, and are obtained crystalline; in the cerium group the basic nitrates are insoluble. By further heating insoluble "superbasic salts," finally the oxides are obtained. The temperatures at which these basic and superbasic compounds are formed vary with the electropositive character of the element, the most electropositive element decomposing last. This fact affords a method of separation which has been very frequently employed.

It is by this method that Marignac has discovered ytterbium and Nilson scandium. On the other hand, Kremers and Balke could not separate Ho and Y by this method. James and Brinton have utilised this method to concentrate earths of the erbium group mixed with yttrium. They recommended this for the separation of a mixture of Er, Ho, Dy and earths less basic than Y.

Literature shows that only the basic nitrates of yttrium and gadolinium (one each) have been mentioned. From an isothermal study of the ternary system of $Y_2O_3-N_2O_5-H_2O$, James and Pratt (*J. Amer. Chem. Soc.*, 1910, **32**, 873) showed that the only basic nitrate of yttrium, stable at 25° in aqueous solution, has the composition $3Y_2O_5.4N_2O_5.20H_2O$. It is stable in air and in the presence of a solution of $Y(NO_3)_3$ and from such a solution it can be recrystallised. It is not affected by alcohol, but is decomposed by water. From a detailed study of gadolinium and its compounds Sarkar (*Ann. chim.*, 1927, **8**, 239) isolated one basic nitrate of the composition $3Gd_2O_3.4N_2O_5.20H_2O$ quite analogous to the yttrium compound, a fact which justifies the position of gadolinium in the yttrium group. Sarkar obtained the compound by heating the hydrated nitrate of gadolinium in a porcelain capsule at 320° when nitrous fumes began to be evolved. After some time when the reaction was over, it was extracted with boiling water or better with a solution of gadolinium nitrate, quickly filtered, and cooled when beautiful crystals separated. Unlike the normal nitrate, the basic nitrate is stable in air and non-hygroscopic. It is insoluble in alcohol and undergoes hydro-lysis on boiling with water.

The analogy of bismuth salts with those of the rare-earths is well known as has been pointed out in a previous communication. This analogy extended to the phase rule study of the system $Bi_2O_3-N_2O_5-H_2O$ leads to the isolation of three basic nitrates of bismuth of the compositions :—(i) $BiONO_3.H_2O$, (ii) $Bi_2O_3.10BiONO_3.9H_2O$, and (iii) $Bi_2O_3.2BiONO_3.H_2O$. In the present paper systematic investigations of the basic nitrates of the cerium earths have been made.

Physico-chemical methods, such as thermometric and conductometric titrations of solution of the nitrates with caustic soda, have revealed the existence of two basic nitrates of each of the cerium earths La, Ce, Pr and Nd analogous to those of bismuth Nos. 1 and 3. $RONO_3$ and R_2O_3, $2RONO_3$ where R stands for La, Ce, Pr, Nd. The first may be called the basic nitrate and the second the so-called superbasic nitrates of the early workers in the rare-earth chemistry.

Thermal decomposition curves of $La(NO_3)_3$, $Pr(NO_3)_3$ and $Nd(NO_3)_3$, also establish the existence of the above two basic nitrates. Such study of the nitrate of cerium has not been possible owing to the oxidation of cerous to ceric state when heated, even in a current of nitrogen or carbon dioxide, the substance becoming yellow in colour, then decomposes very easily even at 100° forming basic ceric nitrate. Hence the basic nitrates of cerous cerium have not been obtained in the solid state like those of the others.

The temperatures of formation and ranges of stability have been studied. These have been found to follow the "serial order" of the rare-earths, lanthanum being the most basic, decomposes at the highest temperature.

EXPERIMENTAL

Conductivity Titrations.

All the measurements were made at 32° in an electrically regulated thermostat by which the temperature could be maintained constant to $\pm 0.1°$.

The solutions ($M/50$, 50 c.c.) of the nitrates were titrated with caustic soda solution ($2M$) taken in a micro-burette, resistances were measured at regular intervals and the reciprocals of the resistances were then plotted against the c.c. of alkali added. The curves reveal two breaks, one corresponding to $RONO_3$ where the ratio of nitrate to NaOH is 1:2 and the other R_2O_3, $2RONO_3$ where the ratio of nitrate to NaOH is 2:5 besides a third break in the region 1:3 corresponding to the hydroxide $R(OH)_3$.

FIG. 1

Conductometric titration curves for NaOH and nitrates of

C.c. of alkali.
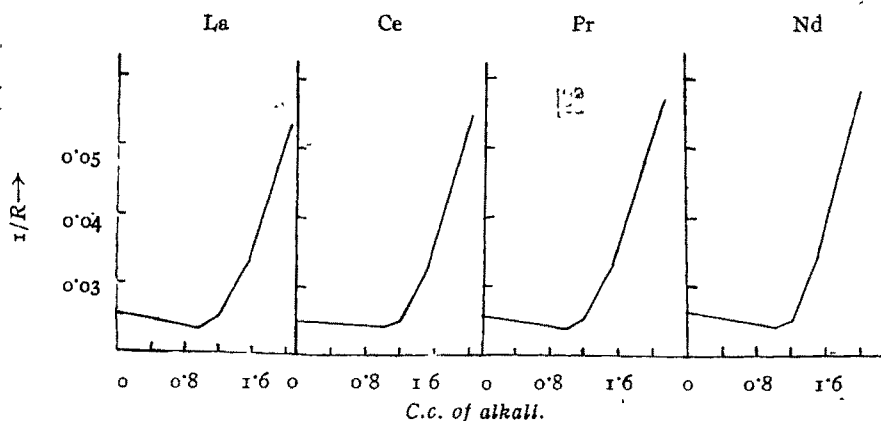
Thermometric Titrations.

The arrangement for thermometric titration consists of one Dewar flask kept within a second Dewar flask. The solution to be titrated is taken in the inner flask. The flask is covered at the top with a three-holed asbestos board; through one hole passes the Beckmann's thermometer reading to the 1/100th of a degree, through the second passes one glass stirrer which is worked mechanically at a low speed, and through the third hole passes the tip of the burette. The burette is kept in a glass jacket of 1½″ diameter packed inside with asbestos rope, only a short length at the top kept exposed for reading the burette. The bottom of the burette outside the jacket is also wrapped with asbestos. The stop-cock of the burette is worked with a wooden clip, not with bare hand.

The technique is due to Dutoit (*J. chim. phys.*, 1921, **19**, 324, 331) who used it for studying besides many other systems the basic salts of aluminium, zinc and magnesium.

The solution (M/10, 40 c.c.) of the nitrates are taken in the inner flask and caustic soda solution (2M) added from the burette at regular intervals and the changes in temperatures noted. The differences in temperature are then plotted against the c.c. of alkali solution added. Here, also, the curve reveals two breaks one corresponding to $RONO_3$ where the ratio of the nitrate to alkali solution is 1:2 and the other in the region R_2O_3, $2RONO_3$ where the above ratio is 2:5 and finally a third corresponding to the hydroxide $R(OH)_3$.

Results for lanthanum, cerium, praseodymium and neodymium nitrates are shown in Fig. 2 ; curves are all of the same type.

FIG. 2

Thermometric titration curves of alkali and
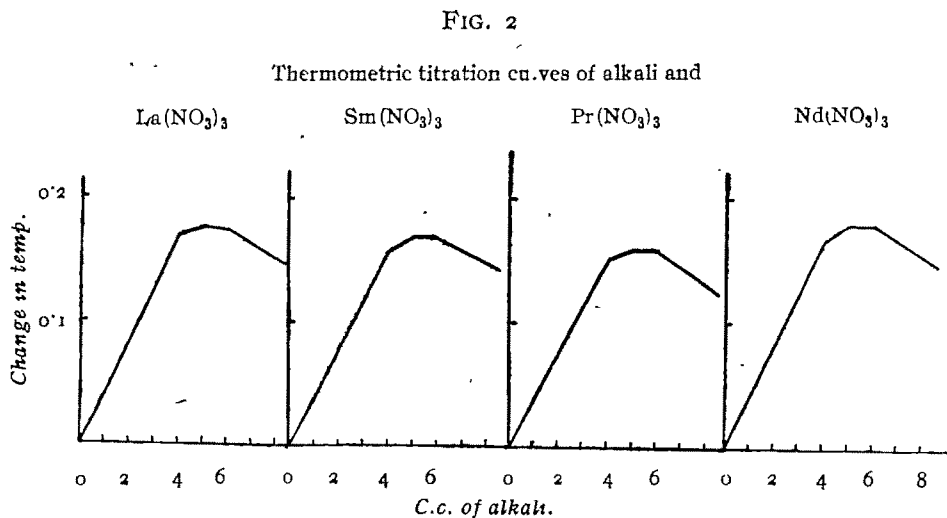
Thermal Decomposition of the Nitrates of the Rare-earths.

The quantitative examination of the decomposition of the nitrates of the rare-earths by the action of heat indicates the existence of different basic nitrates, the

disengagement of nitrous vapours occur in successive steps. For this study, the following experimental arrangement was used. The neutral nitrate was taken in a weighing bottle, and placed in a big hole bored in an aluminium block surrounded by a cement block as a support. A thermometer was placed in a second hole in the aluminium block bored so deep that its bulb lay in the same level with the substance in the weighing bottle. The block was then heated from below with a small gas flame. By this means, the temperature could be kept constant within $\pm 0.5°$ very conveniently particularly when kept inside a fume cupboard.

At first the hydrated nitrate became anhydrous and then began to decompose. The temperature was raised gradually and the weight of the weighing bottle was made constant at each temperature. The losses in weight were then plotted against the temperatures and curves obtained.

Lanthanum Nitrate.—Here a curve with three steps is obtained : the first step corresponds to $LaONO_3$, this is formed at $330°$ and stable up to $350°$. (Found : La, 64.04; HNO_3, 28.83. $LaONO_3$ requires La, 64.05; HNO_3, 29.03 per cent). The

FIG. 3

Thermal decomposition curve.
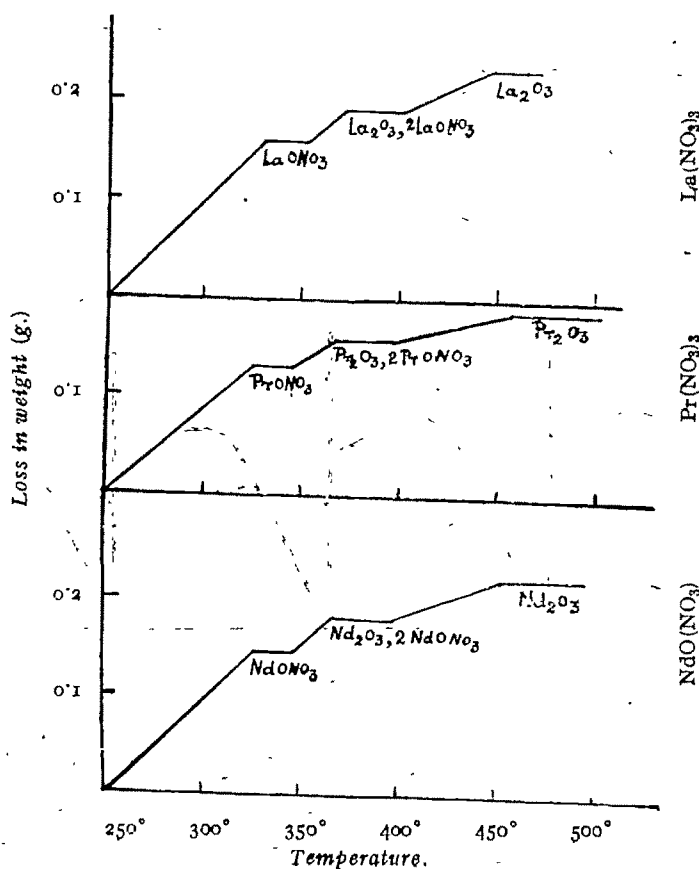
second step corresponds to La_2O_3, $2LaONO_3$, stable between 370° and 400°. (Found : La, 73.00 ;, HNO_3, 16.54. La_2O_3, $2LaONO_3$ requires La, 73.16 ; HNO_3, 16.58 per cent) and finally the trioxide La_2O_3. (Fig. 3).

Praseodymium Nitrate.—Here also a curve with three steps is obtained. The first step corresponds to $PrONO_3$; this is formed at 325° and stable up to 345°. (Found : Pr, 64.26 ; HNO_3, 28.52 ; $PrONO_3$ requires Pr, 64.34 ; HNO_3, 28.76 per cent). The second step corresponds to Pr_2O_3, $2PrONO_3$ formed at 365° and stable up to 390°. (Found : Pr, 73.08 ; HNO_3, 16.25. Pr_2O_3, $2PrONO_3$ requires Pr, 73.44 ; HNO_3, 16.41 per cent) and finally the oxide Pr_6O_{11} a jet black powder obtained when strongly heated.

Neodymium Nitrate.—Here also a very similar curve is obtained. The first basic nitrate corresponds to the formula $NdONO_3$ formed at 325° and stable up to 345°. (Found : Nd, 64.28 ; HNO_3, 28.54 ; $NdONO_3$ requires Nd, 64.54 ; HNO_3, 28.64 per cent). The second basic nitrate, like the others, have the composition Nd_2O_3, $2NdONO_3$ formed at 365° and stable up to 395°. (Found : Nd, 73.38 ; HNO_3 16.18. Nd_2O_3, $2NdONO_3$ requires Nd, 73.58 ; HNO_3, 16.32 per cent) and finally the oxide Nd_2O_3.

All the basic nitrates of these cerium earths are insoluble in water and their aqueous solutions undergo hydrolysis on boiling. The lanthanum compounds are colourless, the praseodymium compounds are faint green almost colourless, while those of neodymium have faint rosy tints.

Method of Analysis.

A weighed quantity of the substance was decomposed with caustic soda solution, the rare-earth hydroxide filtered, dissolved in nitric acid and precipitated with oxalic acid and the oxalate ignited to oxide. The filtrate from the hydroxide, which contained the nitrate was distilled with caustic soda and Devarda's alloy, the liberated ammonia was absorbed in a known quantity of standard acid and the excess of acid was finally titrated with standard alkali.

PHOTOCHEMICAL REACTIONS WITH SOME INORGANIC COLLOIDS AS ACTIVE AGENTS UNDER THE INFLUENCE OF LIGHT IN VARIOUS STATES OF POLARISATION   PART XV. PHOTOCHEMICAL REDUCTION OF CERIC BORATE SOL WITH GLUCOSE AND LAEVULOSE

By T. BANERJEE

Photochemical reduction of the ceric borate sol with glucose and laevulose has been studied in light. Effect of varying concentrations of the reductants and the sol, intensity of radiations, temperature and the influence of polarised light and also the effect of insolating the sol on the light reaction have been investigated and an equation has been developed which can explain the characteristic features of the observed reaction.

The experimental arrangement has been described in Part I (*J. Indian Chem. Soc.*, 1937, **14**, 500).

Pure ceric ammonium nitrate (B.D.H.) and Merck's pure borax after recrystallisation was used for the preparation of the sol, which was prepared after Prakash and Dhar (*ibid.*, 1930, 7, 373) dialysis was continued till the dialysate showed no test of ammonia with Nessler's reagent.

Estimation of Ceric Borate Sol:—A definite volume of the sol was run into 10 c.c. of 4% sulphuric acid contained in a stoppered conical flask. It was then shaken for 1 minute and after 5 minutes titrated slowly with standard ferrous ammonium sulphate solution with constant shaking using one or two drops of diphenylamine (25%) as internal indicator.

The reliability of this method of estimation will be evident from the following potentiometric titrations.

TABLE I

A sample of ceric borate sol was taken and titrated potentiometrically with $0.01N$-FeAmSO$_4$. Amount of ceric borate sol taken was 0.376 c.c.

Amount of titre in c c. (x)	— 0	0 5	0.8	0.85	0 9	0 95	1.0	1.05	1 10	1.20
E M.F. (E)	0.585	0.554	0.498	0 477	0 430	0.355	.0 230	0.236	0.215	0.195
dE/dx	—	6	19	42	94	150	150	88	41	20

The experiment was repeated several times and the maximum value for dE/dx was found when the amount of titre added was 0.95 c.c.

Again 0.376 c.c. of the above ceric borate sol was titrated with FeAmSO$_4$ (0.01N) using diphenylamine as the internal indicator. Titre required for complete reduction was 0.95 c.c.

By concentration of the sol we shall always understand the ceric equivalent of the sample of the sol.

Ceric borate sol was not reduced by glucose or by laevulose for a period of 10 hours in the dark. The sol and glucose or laevulose, when insolated, showed a long induction period followed by an irregular reaction and a photo-stationary state. This irregularity of the reaction and the photo-stationary state have been traced to be due to dissolved atmospheric oxygen which oxidises the reduced sol. Hence pure nitrogen was passed through the reaction mixture for a sufficiently long time before it was exposed to light. Pipetting of solution for titration was done in an atmosphere of pure nitrogen.

TABLE II

Study of the light reaction.

d (thickness of the reaction cell) = 0·5 cm.   Conc. of ceric borate sol = 0·0144M. Conc. of glucose = 2·5%. p_H = 6·9.   Temp. = 29°. γ = 366$\mu\mu$.   Intensity of radiation absorbed = 405 ergs/cm^2/sec.

Time.	Vol. of 0·002 (M) ferrous ammonium sulphate ≡ 18 c.c. of reaction mixture	$k = \dfrac{2}{t\,(\text{sec})}\left\{\dfrac{1}{\sqrt{a-x}} - \dfrac{1}{a}\right\}.$
(a) 0 min.	1·30 c.c	
(b) 240	1·05	Induction period
(c) 310	0·86	$4\cdot7 \times 10^{-8}$ (from b & c)
(d) 380	0·72	$4\cdot7 \times 10^{-8}$ (from b & d)

The reaction was attended with a long induction period. The velocity of reaction with excess of reductant is best explained by the equation,

$$dx/dt = k(a-x)^{3/2}$$

which on integration gives

$$k = \frac{2}{t}\left\{\frac{1}{\sqrt{a-x}} - \frac{1}{a}\right\} \qquad \dots \ (i)$$

TABLE III

Effect of varying the concentration of the reductants.

d (thickness of the reaction cell) = 0·5 cm.   Sol conc. = 0·0144M.

Temp.	I_{abs} in ergs/cm^2/sec.	Reductant used.	Conc. of reductant	k (1) mean.	Quantum yield.
29°	405	Glucose	2·5%	$4\cdot7 \times 10^{-8}$	1·95
29	,,	,,	1·25	3·6	1·65
29	,,	,,	0·625	2·52	1·25
25	1215	Laevulose	2·5	9·4	1·80
25	,,	,,	1·25	5·55	1·05
25	,,	,,	0·625	2·8	0·53

$1/k$ plotted against $1/c$ (reductant) gives a straight line.

TABLE IV

Effect of varying the concentration of ceric borate sol.

$\lambda = 366\mu\mu.$　　$p_\text{H} = 6\cdot9.$　　I_abs in ergs/cm^2/sec. $= 571.$

Temp	Sol. conc.	Reductant used	Reductant conc.	$k(1)$
29°	0·0145M	Glucose	2·5%	5 58 × 10⁻⁸
29	0·0072	,,	,,	·5·32
25·5	0·0144	Leavulose	0 625	·1 9
25	0·0072	,,	,,	1 8

From the above table it is evident that the velocity constant is independent of the sol concentration, under otherwise identical conditions.

TABLE V

Effect of varying the intensity of radiation.

$\lambda = 366\ \mu\mu.$　　$p_\text{H} = 6\cdot9.$　　Sol. conc. $= 0\cdot0144M.$

Temp.	I_abs in ergs/cm^2/sec.	Reductant used.	Conc. of reductant.	$k(1)$
29°	405	Glucose	2·5%	4·7 × 10⁶
29	650	,,	,,	5·67
25·5	1215	Laevulose	0·625	2·8
25·5	2230	,,	,	3 65

The above table shows that the velocity constant is proportional to the square root of the intensity of radiant energy absorbed.

Effect of Varying the Temperature.

The temperature coefficient of the photo-reduction is small, being of the order of 1·1 to 1·2.

TABLE VI

Influence of polarised light.

$\lambda = 366\ \mu\mu.$　　$p_\text{H} = 6\cdot9.$

(a) Sol. conc. $= 0\cdot0144M$; glucose $= 2\cdot5\%$ ·　　　(b) Sol. conc. $= 0\cdot0144M$; laevulose $= 1\cdot25\%$

Temp.	I_abs in ergs/cm^2/sec	Nature of light used.	$k(1)$		Temp.	I_abs in ergs/cm^2/sec.	Nature of light used.	$k(1)$
29°	405	Unpolarised	4·7 × 10⁻⁸		25°	1215	Unpolarised (ordinary)	5·55
,,	290	Plane polarised	3·65		,,	604	Plane polarised	3 72
30	135	d-Circularly polarised	1·35		,,	251	d-Circularly polarised	1·5
,,	135	l-Circularly polarised	2·53		,,	251	l-Circularly polarised.	2·35

It is clear from the above table that on the assumption that square root law holds good, $V_0 = V_\text{P} = V_\text{L} > V_\text{D}$, the terms V_0, V_P, V_L, V_D having the same significance as before.

Effect of Pre-insolating the Sol.

From Table II, the reaction seems to possess an induction period of about 3 hours; for weak illumination it is even 6 hours.

The sol was insolated for nearly four hours in a quartz test tube, in an atmosphere of nitrogen gas and then mixed with other constituents of the reaction mixture and exposed to light (366 $\mu\mu$). The reaction is now marked by the absence of any "induction period." That the velocity constant also remains unaffected is shown by the following data.

TABLE VII

Conc. of sol $= 0.0144M$. Conc. of glucose $= 2.5\%$. Intensity of radiation absorbed $= 405$ ergs/cm^2/sec.

Time.	Titre.	$k(1) \times 10^5$.	$k_{mean}(1) \times 10^5$.
0 min	1.22 c c		
50	1.04	4 75	
104	0 90	4.65	
			4.7

When the sol was not preactivated the velocity constant was also 4.7×10^{-5} (Table II). It has been observed that the active sol does not react with glucose or laevulose in the dark. The activation does not take place in an atmosphere of ordinary air. The active sol looses its activity within half an hour in the dark. Pre-insolation of the glucose and laevulose cannot avoid the induction period.

Very dilute (0.0002M) ferric chloride, ferrous ammonium sulphate, copper sulphate, and manganous sulphate have practically no influence on the velocity constants of the reactions.

DISCUSSION

Any mechanism proposed for the photo-oxidation of glucose and laevulose by sol of ceric borate should be in a position to explain the following characteristic features :—

(i) That the velocity of reaction is proportional to the 3/2th power of the concentration of the photoactive reagent,

(ii) that the velocity constant varies as the square root of intensity of absorbed radiation under otherwise identical experimental conditions,

(iii) that the inverse of velocity constant plotted against the inverse of concentration of reductant is a straight line,

(iv) that the quantum efficiency is generally greater than unity which indicates the existence of some kind of chain mechanism.

The mechanism of oxidation of sugars by air in presence of cerous hydroxide gels has been studied by Ghosh and Rakshit (*J. Indian Chem. Soc.*, 1935, **12**, 357). There the formation of ceric hydroperoxide in course of oxidation of sugars was experimentally demonstrated. It appears that a ceric compound activated by absorption of radiation is not capable of reacting according to the simple mechanism.

Ceric compound (activated) $+ AH_3$ (substrate)$\longrightarrow$cerous compound$+ H^+ + AH$.
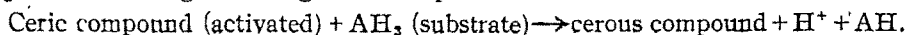
If that were so, the kinetics of photo-oxidation would have been extremely simple. The fact is that the substrate AH_2 cannot part with its hydrogen atoms singly; whenever it enters into any reaction both the hydrogen atoms must be removed simultaneously. A mechanism which takes into consideration this central fact, and also the intermediate existence of ceric hydroperoxide compound, may be developed as follows :—

(i)   A molecule of ceric compound $[Ce^{+-+}] + h\nu \longrightarrow$ activated molecule $(Ce^{++++}act.)$

(ii) $Ce^{++++}act. + Ce^{++++}normal + 2H_2O \longrightarrow$ cerous compound + ceric hydroperoxide.

(iii)   Ceric hydroperoxide + AH_2 + ceric compound $\longrightarrow$ A + cerous compound + active ceric compound.

(iv)   2 Activated ceric compound molecules + $AH_2 \longrightarrow$ A + 2 cerous compound molecules.

It is easily seen that this mechanism will give us the following value of velocity of reaction if reaction (iv) is, as is very probable, small compared with reaction (iii).

$dx/dt = k_1[Ce^{++++}act.][Ce^{++++}normal].C_s$, where C_s is the surface concentration of the reductant on the colloid micelle.

$$= k_2 \left[\frac{I_{abs} \text{ by } Ce^{++++}}{Nh} \right]^{\frac{1}{2}} . [Ce^{++++}] \ C_s.$$

Our experiments on the measurement of the extinction coefficients of radiations 366 $\mu\mu$ by ceric and cerous borate sols, show that these magnitudes are of the same order. Hence we may assume that of the total light (I_{abs}) absorbed by the system, $I_{abs}(a-x)$, is the fraction absorbed by the ceric compound.

Hence $dx/dt = k_2 \sqrt{I_{abs}} \ (a-x)^{8/2} . C_s$

The surface concentration of the reductant glucose is given by the well known Langmuir equation

$$C_s = \frac{k_3 c(\text{bulk})}{k_4 + k_3 c(\text{bulk})}.$$

The equation thus developed explains at once the characteristic features of the reaction which we have observed. In view of the chain mechanism postulated in reactions (ii) and (iii) and the break in the chain due to reaction (iv), the probability of the quantum efficiency being greater than unity is indicated.

The difference in the efficiencies of these photochemical reactions in circularly polarised light can be best explained from our knowledge of the anisotropic factor for ceric borate sol in the region of 366 $\mu\mu$ (Ghosh and Banerjee, *Kolloid Z.*, 1939, **86**, 3).

Conc. of ceric borate sol 0·0032 M	I_{abs} = 570 ergs/cm²/sec.	Anisotropic factor for λ = 366 $\mu\mu$
	Period of preexcitation = 12 hours. d-Circularly polarised light. l Circularly polarised light.	$g = \dfrac{Al - Ad}{\frac{1}{2}(Al + Ad)}$ −0·0401 +0·0261

CHEMISTRY OF THE RARE-EARTHS. PART V.
BASIC NITRATES OF YTTRIUM EARTHS

By NIHAR KUMAR DUTT

Basic nitrates of Yt, Yb and Gd have been studied and each has been shown to give a soluble basic nitrate of the composition $3R_2O_3, 4N_2O_5$. Gadolinium has, in addition, been found to give an insoluble basic salt $GdONO_3$ similar to those for cerium earth and bismuth as expected from its position in the series.

Yttrium, as has been shown by James and Pratt (*J. Amer. Chem. Soc.*, 1910, **82**, 873) gives only one basic nitrate of the composition $3Y_2O_3.4N_2O_5,20H_2O$, soluble in water. Thermometric and conductometric titration curves of yttrium nitrate with caustic soda solution obtained by the present author also reveal the existence of only one basic nitrate of the above composition. To see whether this is a common characteristic of the elements of the yttrium group, the basic nitrate of ytterbium has been studied. The conductometric titration of ytterbium nitrate with caustic soda solution gives a curve analogous to that of yttrium nitrate with caustic soda, showing only one basic nitrate $3Yb_2O_3, 4N_2O_5$ of similar composition, which therefore appears to be characteristic of the elements of the yttrium group.

While studying gadolinium and its compounds Sarkar (*Ann. chim.*, 1927, **8**, 239) isolated a basic nitrate of the composition $3Gd_2O_3, 4N_2O_5.20H_2O$ soluble in water and perfectly analogous to that of yttrium. It is to be expected, however, from its position in the "serial order" of the rare earths, that gadolinium should possess properties characteristic of both cerium and yttrium groups, for example,

(*i*) Gadolinium gives an acid tartrate of the composition $HGd(C_4H_4O_6)_2.2H_2O$ similar to the corresponding salt of bismuth.

(*ii*) The basic nitrate $3Gd_2O_3, 4N_2O_5, 20H_2O$ is analogous to the corresponding salt of yttrium.

(*iii*) The addition product of gadolinium nitrate with antipyrine of the composition $Gd(NO_3)_3, 3C_{11}H_{12}ON_2$ resembles those of the cerium group.

(*iv*) The compound of gadolinium nitrate with hexamethylene tetramine has the composition $Gd(NO_3)_3. 2C_6H_{12}N_4,10H_2O$ analogous to those of the yttrium group elements.

(*v*) Gadolinium platinocyanide crystallises with 18 molecules of water of crystallisation, characteristic of the cerium group—those of the yttrium group crystallise with 21 molecules of water; its colour, however, is cherry-red with beautiful green fluorescence characteristic of yttrium group. Those of cerium group have yellow colour with blue fluorescence.

A detailed study of the basic nitrates of gadolinium has therefore been made by the present author to see whether there exists also any basic nitrate analogous to those of cerium group elements. Conductometric titration curve of gadolinium nitrate with caustic soda solution as well as the thermal decomposition curve of gadolinium nitrate with increasing temperature have revealed the existence of two basic nitrates—the first having the composition $3Gd_2O_3. 4N_2O_5$ previously described by Sarkar (*loc. cit.*) analogous to the corresponding salt of yttrium, soluble in water, and second of the composition $GdONO_3$ not previously described and analogous to that of bismuth and cerium earths, insoluble in water.

EXPERIMENTAL

Purification of Yttrium Nitrate.—Yttrium nitrate available in the market supplied by Kahlbaum was used as the starting material. The mean equivalent weight has been determined and found to be 114.5. It contains besides yttrium small quantities of other yttrium earths like Dy, Ho and Er and also a little of the cerium earths. Separation of the latter is best assured by the known method of separation with sodium sulphate. For this purpose finely powdered anhydrous sodium sulphate is added to the solution of the nitrate or chloride while hot under stirring, till a portion of the test solution does not show any absorption band of Nd. The solution is freed from alkali salts by precipitation with ammonia then redissolving in nitric or hydrochloric acid. The remaining yttrium earths having absorption, *viz.* Dy, Ho and Er is removed by the ferricyanide method of Prandtl (*Z. anorg. Chem.*, 1938, **238**, 328). For this purpose, to a not too dilute neutral or neutralised solution was added concentrated warm potassium ferricyanide under stirring from which after allowing to stand for some time, the absorption lines of Ho and Er completely disappeared from the solution. From the filtrate of the ferricyanide, yttrium was precipitated with caustic soda as hydroxide, washed, dissolved in HCl or HNO_3 and the concentrated solution examined spectroscopically for absorption. The still remaining Yt earths containing Dy, Ho, and Er were removed by treating again with K_3FeCy_6 and remaining cerium earths by precipitation with sodium sulphate. For final purification, the differential decomposition of the nitrate was utilised. For this purpose, the nitrate was heated in a porcelain basin at 300° till the mass took a steely appearance. It was then extracted with hot water and allowed to crystallise, when yttrium was obtained as its basic nitrate in microcrystalline form. The purity of the substance was tested spectroscopically when only mere traces of gadolinium were detected. The purity was further tested by the determination of the atomic weight from the ratio $Y_2(SO_4)_3, 8H_2O:Y_2O_3$ and this has been found to be 89.5.

Purification of the Ytterbium Fraction.—Ytterbium fraction of unknown origin was used as the starting material. It contained besides ytterbium, its neighbours thulium and lutecium and very little of the cerium earths. The latter were removed by precipitation with sodium sulphate. From the filtrate the rare-earth was precipitated twice with ammonia as hydroxide, washed free of alkali salts, dissolved in HCl and precipitated with oxalic acid; the oxalate was then ignited to oxide and the oxide was dissolved in acetic acid to convert it into acetate. The final purification was made according to the method of Marsh (*J. Chem. Soc.*, 1943, 8). The method consisted in the reduction of $YbAc_3$, with sodium amalgam and subsequent formation of ytterbium amalgam since its neighbours are devoid of amalgam forming power. For this purpose the acetate was dissolved in the least quantity of boiling water and was treated hot with sodium amalgam, the solution was made weakly acid to prevent the formation of hydroxide. The amalgam was then treated with excess of hydrochloric acid and ytterbium precipitated as oxalate and the latter ignited to oxide. The purity of the sample was tested by determination of the atomic weight from the ratio $Yb_2(SO_4)_3, 8H_2O : Yb_2O_3$ and this was found to be 172.5.

Thermometric Titration : Yttrium Nitrate and Caustic Soda.

Experimental arrangements were the same as presented in a previous communication (*J. Indian Chem. Soc.*, 1945, **22**, 75).

The solution ($M/10$) of yttrium nitrate (40 c.c.) was taken in the inner flask and caustic soda solution ($2M$) was added from the burette at regular intervals and changes in temperature noted. The differences in temperature were then plotted against the volume of alkali solution added. Here, the curve, unlike those for the elements of the cerium group (*cf*. Part III of this series), shows one break corresponding to $3Y_2O_3$, $4N_2O_3$ where the ratio of the nitrate to alkali is 1 : 1·667 corresponding to that of James and Pratt (*loc. cit.*) besides a second one corresponding to the hydroxide $Y(OH)_3$ where the above ratio is 1 : 3. Results appear in Fig. 1.

FIG. 1

Thermometric titration curve
$Y(NO_3)_3$.

FIG. 2

FIG. 3

FIG. 4

$Y(NO_3)_3$+NaOH.

$Yb(NO_3)_3$+NaOH.

Gd nitrate+NaOH.
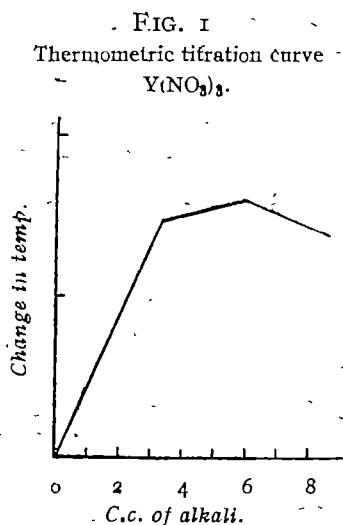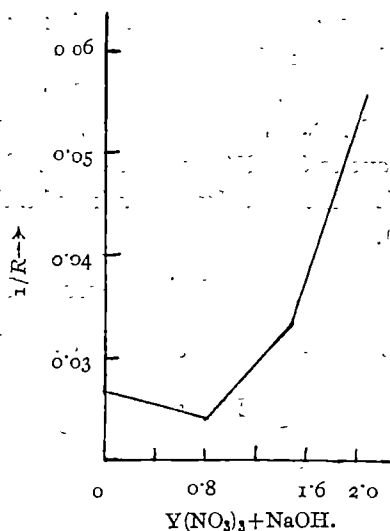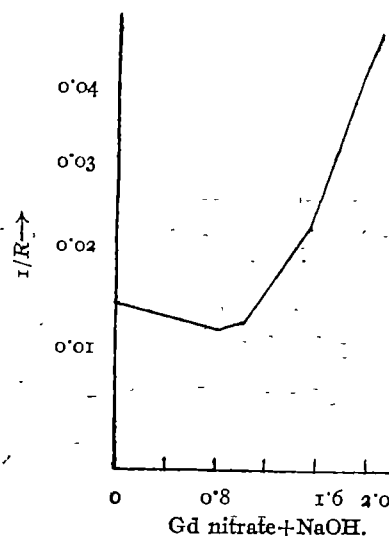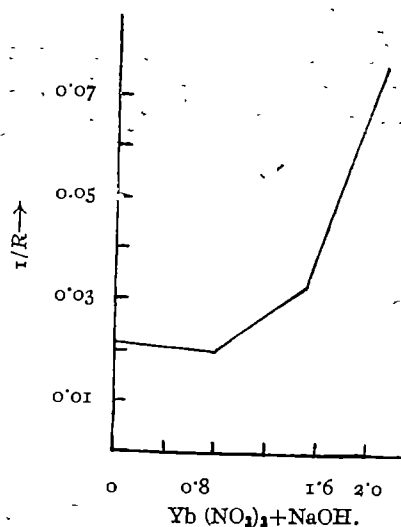
Conductometric Titrations.—All measurements were made at 32° in an electrically regulated thermostat. $M/50$-solution of the nitrates and $2M$ solution of alkali were used. Experimental arrangements were the same as given in Part IV of this series (*loc. cit.*).

Yttrium Nitrate and Caustic Soda.—Here a curve was obtained with one break corresponding to $(3Y_2O_3, 4N_2O_5)$ that of James and Pratt (*loc. cit.*) and a second one corresponding to the hydroxide $Y(OH)_3$. Results obtained are very similar to those obtained by the previous physical method (Fig. 2).

Ytterbium Nitrate and Caustic Soda.—A curve, very similar to the previous one, was obtained with one break corresponding to $3Yb_2O_3, 4N_2O_5$ where the ratio of the nitrate to caustic soda is $1:1·67$ besides that for the hydroxide. The results clearly indicate that the above basic nitrate is characteristic of the yttrium group elements which is of a type quite different from the basic nitrates of the cerium group elements (Fig. 3).

Gadolinium Nitrate and Caustic Soda.—The curve obtained in this case reveals three breaks in all as in the case of the cerium earth elements, with this difference that here the first break corresponds to $3Gd_2O_3, 4N_2O_5$ described by Sarkar (*loc. cit.*), the second one to $GdONO_3$ characteristic of those of first series of basic nitrates of cerium earth elements and also bismuth and a third corresponding to the hydroxide $Gd(OH)_3$ (Fig. 4).

Thermal Decomposition of Gadolinium Nitrate.

Experimental arrangements were the same as described in Part IV of this series. On plotting the loss in weight of the nitrate of gadolinium against the constant temperatures, a curve is obtained with three steps. The first step corresponds to $(3Gd_2O_3, 4N_2O_5)$ that described by Sarkar](*loc. cit.*); this is formed at 310° and stable up to 320°. The second step corresponds to $GdONO_3$ analogous to the first basic nitrate of the cerium earth elements not previously described. This is formed at 330° and stable up to 350°. {Found: Gd, 66·48; HNO_3, 26·65; $GdONO_3$ requires Gd, 66·81; HNO_3, 26·81 per cent}. The third corresponds to Gd_2O_3 (Fig. 5).
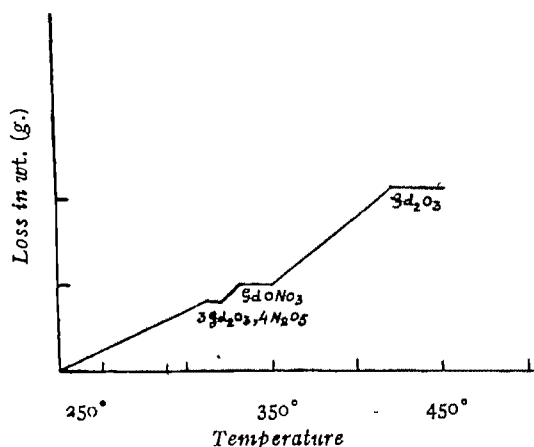
FIG. 5

Loss in wt. (g.)

Gd_2O_3

$GdONO_3$

$3Gd_2O_3, 4N_2O_5$

250° 350° 450°

Temperature

The author's best thanks are due to Dr. P. B. Sarkar for his kind interest and laboratory facilities.

PARACHOR AND RING STRUCTURE. PART II

By W. V. Bhagwat and S. O. Shukla

It is suggested that bridge-ring may be considered to be equivalent to three rings and not two rings. It is shown that in case of o-toluquinone the tautomerism between simple and bridge ring does exist unlike the conclusion of Sugden. Further phorone and its derivatives which form dicyclic structure should contain one ring of three and one of four and not one of three and one of five. The same is true of distyryl ketone. Hence dichloro derivatives of phorone seem mainly to be bicyclic in form unlike the conclusions of Sudgen.

Most of the reactions of p-quinones are represented by the formula (I) but Grabe (*Annalen*, 1868, **146**, 1), Binder (*Chem. Ztg*, 1921), Hartley and Leonard (*J. Chem. Soc.*, 1909, **95**, 34) and Haakh (*J. prakt. Chem.*, 1910, **82**, 546) prefer the peroxide formula (II).

$$
\begin{array}{cc}
\text{HC}\!-\!\text{CH} & \text{HC}\!-\!\text{CH} \\
\text{O}=\text{C}\big\langle\quad\big\rangle\text{C}=\text{O} & \text{C}\big\langle\!=\!\big\rangle\text{C} \\
\text{HC}\!-\!\text{CH} & \text{HC}\!-\!\text{CH} \\
\text{(I)} & \text{(II)}
\end{array}
$$
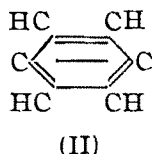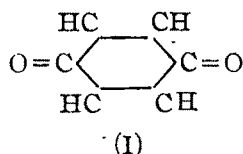
Sugden ("Parachor and Valency," p. 46) comparing his parachor values of benzoquinone and toluquinone in fused state concludes that they should have diketone structure (I) and that if tautomerism between (I) and (II) occurs then the amount of (II) present in fused state is very small.

Sugden considers that the peroxide structure is in one plane and hence contribution is due to two rings of six only. In our opinion if the structure is considered in space then the contribution due to three rings,

$$
\begin{array}{ccc}
\text{HC}\!-\!\text{CH} & \text{O}\quad\text{O} & \text{HC}\!-\!\text{CH} \\
\text{C}\big\langle\quad\big\rangle\text{C}, & \text{C}\big\langle\quad\big\rangle\text{C}, & \text{C}\big\langle\quad\big\rangle\text{C} \\
\text{O}\cdot\text{O} & \text{HC}\!-\!\text{CH} & \text{HC}\!-\!\text{CH}
\end{array}
$$
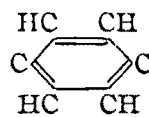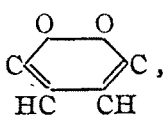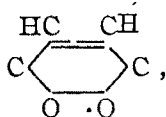
must be added. The calculated parachor for peroxide formula is therefore to be increased by 6·1. The results still favour the diketone structure, but they no doubt support the view that tautomerism between the forms (I) and (II) does exist even in the fused state, specially in the case of toluquinone and that at least 28% of the substance are in peroxide from, even at the temperature of fusion. It is not unlikely that at ordinary temperature the view of Grabe and others (*loc. cit.*) is more correct. The deviation in part may be due to the fact that the additive nature of ring structure shown in Part I may not be exactly true, as all the three rings are not identical six-membered rings.

Another structural problem is the tautomerism of the derivatives of phorone studied by Francis and Willson and by Ingold and Shoppy (*J. Chem. Soc.*, 1913, **103**, 2238; 1928, 365, 1662, 1868). If substituents X and X' are introduced into α-position in the phorone molecule, a rearrangement of valencies may take place to give bicyclic structure. If,

however, one of the substituent groups is of the form YO a monocyclic structure may result as shown below :—

$$O=C\begin{cases}CH\!=\!\!=\!C.Me_2\\CH\!=\!\!=\!C.Me_2,\end{cases}\qquad O=C\begin{cases}CX\!=\!\!=\!C.Me_2\\CY\!=\!\!=\!C.Me_2\end{cases} \rightleftharpoons O=C\begin{cases}CX\!-\!\!-\!C.Me_2\\CY\!-\!\!-\!C.Me_2\end{cases}$$

$$O=C\begin{cases}CX\!=\!\!=\!C.Me_2\\C\!=\!\!=\!C.Me_2\\ \ OY\end{cases} \rightleftharpoons YO-C\begin{cases}CX\!-\!\!-\!C.Me_2\\C\!-\!\!-\!C.Me_2\\ \ O\end{cases}$$
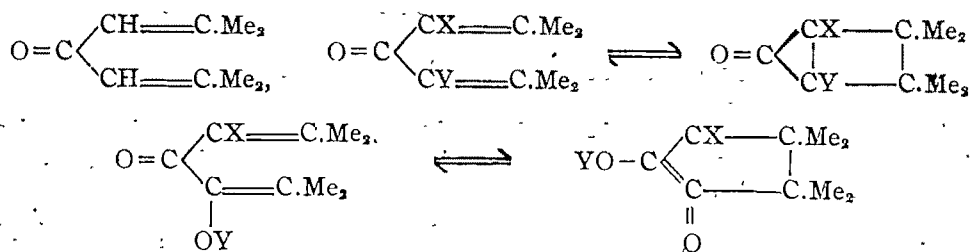
Sugden (*J. Chem. Soc.*, 1928, 490) has compared the calculated and observed values for various substituents in X and Y position.

In case of bridge-ring structure Sugden (*loc. cit.*) assumes that they are equivalent to two rings, one of five and one of three members. Whether the structure is considered in space or in one plane, there is one ring of three and one of four. Hence the difference between open chain and ring structure for bicyclic formula for the calculated values of parachor should be P(ring of three) + P(ring of four)$-2P$(double bond). This is equal to $16{\cdot}7+11{\cdot}6-46{\cdot}4=18{\cdot}1$ and not $21{\cdot}4$ as calculated by Sugden. In a similar manner difference between monocyclic structure and open chain structure is $-14{\cdot}7$. When both types of rings are possible and the value lies between the two, $-18{\cdot}1$ and $-14{\cdot}7$, it is difficult to choose between the two, since both values are so near each other. The difference for dichlorophorone is $-18{\cdot}9$. This in our view clearly indicates that it is in all probability bicyclic in structure and not a tautomeric mixture of isomerides represented by the structures :

$$O=C\begin{cases}C.Cl\!=\!\!=\!C.Me_2\\C.Cl\!=\!\!=\!C.Me_2\end{cases} \rightleftharpoons O=C\begin{cases}C.Cl\!-\!\!-\!CMe_2\\C.Cl\!-\!\!-\!CMe_2\end{cases}$$
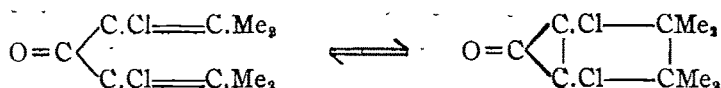
In other cases when the Y group is of the type OY, all values indicate bicyclic structure although Ingold and Shoppe (*loc. cit.*) believe that all of them have monocyclic structure on chemical grounds.

Derivatives of distyryl ketone show similar bicyclic change. Thus dibromodistyryl ketone gives an anomaly of $-13{\cdot}1$ very near to $-18{\cdot}1$ indicating the predominance of the bicyclic form. In this case also Sugden assumes the existence of one ring of three and one of five. As stated above there is one ring of three and one of four members.

$$O=C\begin{cases}CBr\!=\!\!=\!CH.C_6H_5\\CBr\!=\!\!=\!CH.C_6H_5\end{cases} \rightleftharpoons O=C\begin{cases}CBr\!-\!\!-\!CH.C_6H_5\\CBr\!-\!\!-\!CH.C_6H_5\end{cases}$$

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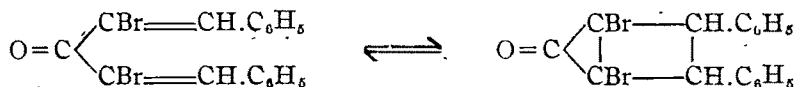
PARACHOR AND RING SRTUCTURE. PART III

By W. V. Bhagwat, S. O. Shukla and S. N. Kaweeshwar

Structure of diacetyl acetone and pyrone and its derivatives is considered on electronic basis. Parachor values contradict the view of Deshapande and co-workers and suggest that pyrone and diethyl pyrone have bridge ring structure, while dimethyl pyrone has simple ring structure. Structure of diacetyl acetone is similarly discussed.

Deshpande, Kaweeshwar and Bhagwat (*J. Indian Chem. Soc.*, 1942, **19**, 155) have determined and calculated the parachor of diacetyl acetone in ethyl acetate assuming that the contribution is due to two rings of five. But as explained in Part II the contribution due to a third ring of six must be added. This makes the bridge ring value 334·1 and not 328, but fails to decide between open chain and closed chain bridge structure. The value 340·3 for closed chain enol form is equally far off from the observed value 324.

Electronic structure requires the existence of singlet linkages and semi-polar bond
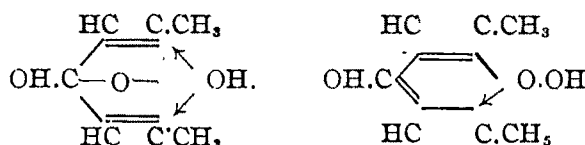
The calculated value of parachor of the keto-form assuming three rings is 309·3 since each ringlet has parachor −12·4. For enol ring the value is 315·6 as there is one semi-polar bond. The open chain value is equally nearer the observed value. Hence the parachor results support the view that diacetyl acetone is a tautomeric mixture of the two enolic forms.
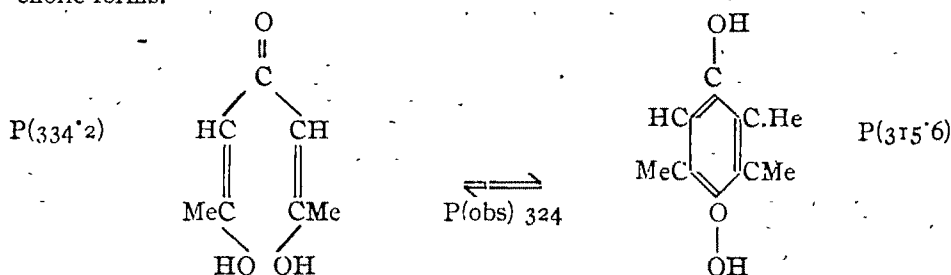
In case of isonitrosocamphor Deshpande, Kaweeshwar and Bhagwat (*loc.cit.*) have given an incorrect value for its calculated parachor as 438. Actually this is 425·2 assuming only two rings of five. The observed value is 438, their conclusion therefore that the bridge ring in isonitrosocamphor corresponds to two rings of five is incorrect. When the structure is considered in space there is one more ring of six, which makes the parachor value 431·2 This is nearer the observed value than the value based on two rings.

Camphor also contains bridge ring, the values on the basis of two and three rings are 381·8 and 387·9 while the observed result is too low to justify any inference. Our results with the parachor of camphor in ethyl acetate are presented in Table I.

Deshapande, Dingankar and Kokil (*J. Indian Chem. Soc.*, 1934, **11**, 592) have discussed the structure of pyrones and its derivatives which may have simple ring structure or bridge structure as suggested by Collie.

Deshapande, Kaweeshwar and Bhagwat have determined the parachors of the above. The values are given in Table II.

TABLE I

$x =$ molar fraction of camphor.

Temp.	d of soln.	Surface tension.	P obs. in soln.	P camphor (obs.).	x
20°	0·9272	25·85	254·1	364·2	0·257
30	0·9182	24·66	253·7	362 7	
40	0 9086	24·35	255·4	369·0	
20	0·9283	25·98	247·3	362	0·217
30	0·9189	24·10	246·4	359	
40	0·9057	23·45	247·4	361	
50	0·8995	22·54	246·8	359	
60	0·8892	21·74	247·4	361	
20	0·9328	26·39	266·3	364·9	0·338
30	0·9236	25·58	266 9	366	
40	0·9152	24·70	267·0	367	
50	0·9086	23·29	265 1	362	
60	0·8966	22·61	266·8	366	—

TABLE II

Substance.	P (obs.).	P (calc.) simple ring.	P (calc.) bridge ring.
Pyrone	195	208·1	219
Dimethyl pyrone	309	286·1	297
Diethyl pyrone	355	364 1 (359)	375 (370)

Their calculated values for diethyl pyrone as; 59·1 and 370· are corrected by us. From the results they conclude that diethyl pyrone and pyrone have simple ring structure while dimethyl pyrone has bridge ring structure, assuming that bridge ring consists of two rings. The values for Collie's structure for dimethyl pyrone and diethyl pyrone should therefore each be increased by 6·1 on the basis of three rings. However the conclusions remain unaffected.

Collie's formulae when considered from electronic stand point, reveals that pyrones contain only two double bonds and the third double bond is really a semi-polar bond.
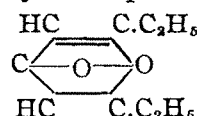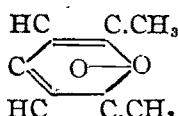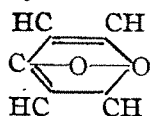
The values obtained with these structures are as follows.

TABLE III

Substance.	P (obs).	P (calc) (2 rings of 5)	P (calc.). (3 rings)
Pyrone	195·0	194·2	200·3
Dimethyl pyrone	309·	272·2	278·3
Diethyl pyrone	355	350·2	356·3

The consideration of 3 rings gives closer approximation with experimental values. Further the bridge ring formulae agree better, with the experimental results in case of pyrone and diethyl pyrone, while dimethyl pyrone gives better results with simple ring structure.

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PARACHOR AND RING STRUCTURE. PART IV

By W. V. BHAGWAT AND S. O. SHUKLA

The parachor of benzene ring by the method of Gibling has been calculated and comes out to be practically zero.

Gibling (*J. Chem Soc.*, 1941, 299) has discarded Sugden's values for atomic and structural parachors and suggested his own values. However, his work is only limited to some of the aromatic homologous series. In this paper we have tried to calculate the value for benzene ring. E. C. denotes "expansion correction" and S. V. denotes "standard values" as calculated by us by his method. The observed values for the parachor of the substances are taken from "A list of Parachors" (*Brit. Assoc. Rep.*, 1932). The values are as recorded below.

TABLE I

Substance	S.V.	E.C.	$P_{calc.}$	P_{obs}	Mean diff %
Benzene	205·8	0 4	206 2	206-206 3	0·0
Toluene	243·4	0·6	244 0	245-246·9	−0·8
Ethylbenzene	283·2	0·8	284·0	283-284	+0·2
n-Propylbenzene	323·0	1·0	324·0	322-323·1	+0·4
n-Butylbenzene	362·8	1·3	364·1	361·7	+0·7
n-Amylbenzene	402·6	1·6	402·2	402·0	+0·5
n-Hexylbenzene	442·4	1·9	444·3	442·0	+0·5
Benzaldehyde	255·6	0·6	256·2	254-256·2	+0·4
Acetophenone	294·3	0·8	295·1	293·8	+0·5
Methyl benzoate	309·8	0·9	310·7	310 4	+0·1
Ethyl cinnamate	418·2	1 6	419·8	417·2	+0·6
Methyl cinnamate	378·4	1·4	379·8	373·9-385·2	+0·08
Diphenylmethane	416·2	1·7	417 9	414·5-419	+0·2
Benzophenone	427·3	1·8	429·1	428 2	+0·2
Benzil	478·2	2·2	480·4	480·8	−0·08
Xylene	281·9	0·8	282·7	283·3-284	−0·3
Mesitylene	318·5	0·9	319·5	320·5	−0·3
p-Ethyltoluene	320·8	0 9	321·7	320·8	+0·3
p-Cymene	358·4	1·2	359·6	357-360·7	+0·2
Tetramethylbenzene	356·2	1·2	357·4	355·6	+0·5

In the case of *cyclo*hexane and *cyclo*hexanone the following values are obtained :

Substance	S.V.	E.C.	$P_{calc.}$	$P_{obs.}$	Mean diff. %
*cyclo*Hexane	238·8	0·55	239·35	239·3-241·8	−0·5
*cyclo*Hexanone	249·9·	0·6	250·5	251 4	−0·3

The coincidence between calculated and observed parachors shows that the contribution of benzene ring towards parachor is practically negligible. In case of *cyclo*hexane and *cyclo*hexanone although the nature of the ring is slightly different (as there are no double bonds) yet there is a close agreement between calculated and observed values, indicating that contribution of six-membered ring towards parachor is practically zero. However, certain anomalies have also been observed as shown below.

TABLE II

Substance.	S.V.	E.C.	$P_{calc.}$	$P_{obs.}$	Mean diff. %
Dibenzylethane	456·0	1·9	457·9	449·8	+1 5
Diphenylpropane	495·8	2·3	498·1	484·5	+2·8
Pentamethylbenzene	393·8	1·5	395·3	390·0	+1·4

These anomalies may be due to slight inaccuracies in the determinations of parachors. The values for the observed parachor are in general smaller than the calculated values and hence the benzene ring, if it has any value, will be negative By following general procedure, that is, by subtracting calculated values from mean observed values we get for parachor of benzene ring a value=(−0·55). This value when substituted gives smaller percentage error, in general below 0·5%. However the error possible in the observed values is almost 0·5% as suggested by Sugden. The error observed with parachor of six-membered ring=0 is also of the same order of magnitude. It is interesting to observe that the benzene itself gives the ring value=0.

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CHEMICAL EXAMINATION OF THE SEEDS OF *AMARANTHUS GANGETICUS*. PART I. THE FATTY OIL FROM THE SEEDS

By N. Chidambaram and R. Ramachandra Iyer

The physical and chemical constants of the oil obtained from the seeds of *amaranthus gangeticus* have been determined and the saturated and the unsaturated fatty acids obtained by the saponification of the oil have been examined.

Amaranthus Gangeticus is a variety of amaranthus of the family 'Amaranthaceae", indigenous to South Travançore. Although this plant is very common and yields a considerable crop of a small seed little information is available regarding the nature of the fatty oils which might be obtained from this source. The only published work is on the oil from the allied species *A. Rotroflexus* (Christensen and Muller, *J. Amer. Chem. Soc.*, 1941, **63**, 2272).

EXPERIMENTAL

6 Kg of the seeds were collected under the personal supervision of the authors, and the dried sample was crushed and repeatedly extracted with petroleum ether (b. p. 50—60°) in the Soxhlet. The petrol was distilled off and the resulting light yellow oil when dried, weighed 360 g., yield 6%.

TABLE I

Physical and Chemical constants of the Oil.

Sp. gravity (29°)	0·9021	Mean M. W. of saturated acids	264·5
Refractive Index (Abbe) (28°)	1 4733	Iodine value of unsaturated acids	106·4
Iodine value (Wijs)	76·3	Iodine value of saturated acids	2 6
Saponification value	175·6	Acid value	12·4
Unsaturated acids (basis of oil)	71 12%	Acetyl value	19·7
Saturated acids (basis of oil)	22·88%	Reichert Meisel value	0 71
Mean M W. of unsaturated acids	283 0	Polenske number	0·50
		Unsaponifiable matter	2·6%

The oil was saponified in the usual manner, the unsaponifiable matter extracted with ether and the fatty acids were liberated The mixture of the fatty acids was then separated into saturated and unsaturated acids by the Twitchell's lead salt-alcohol method (*Ind. Eng. Chem.*, 1921, **12**, 806) and their percentage and constants found (*vide* Table I).

Examination of the Unsaturated Acids.

About 3 g. of the liquid were oxidised with alkaline permanganate at 0°. From the precipitated oxidised acids 9 : 10-dihydroxystearic acid (mixed m. p. with authentic specimen, 132°) and tetrahydroxystearic acid (m.p. 156°) have been obtained thus showing the presence of mainly oleic and linolic acids in the oil.

The quantitative estimation was done by the method, adopted by Jamieson and Baughman (*J. Amer. Chem. Soc.*, 1929, **42**, 1198). A known weight of the unsaturated acids was dissolved in 150 c.c of dry ether and treated with excess of bromine at −10° to −5°. On standing at this temperature for a long time no insoluble bromide separated showing the absence of linolinic acid. The excess of bromine was removed with thiosulphate and the ether evaporated off. The residue from the above was taken up with about 200 c.c. of dry petroleum ether and kept overnight. Linolic tetrabromide separated

as fine glistening star-shaped needles, which weie filtered off, washed and dried (m. p. 111°). On concentrating the mother-liquor, a further crop of tetrabromide was obtained which was added to the first and the total weight determined. Finally the petroleum ether filtrate was evaporated to dryness and the bromine content of the residue determined.

TABLE II

Peicentage of the components.

Acids.	In unsaturated acids	In mixed acids	In original oil
Oleic	61·54	46 5	43·7
Linolic	38 46	29 1	27 3

Examination of the Saturated Acids.

The mixture of the saturated acids was converted into their methyl esters ; and 16 g. of the mixed esters were fractionally distilled under reduced pressure. The saponification equivalents of the various fractions were found out. The acids weie liberated from the different fractions and characterised by their melting points and pieparation of derivatives.

TABLE III

B. p at 5 mm. pressure.	Wt.	Sapon. equiv.	B p. at 5 mm pressure.	Wt	Sapon. equiv.
S_1 148—152° (nearly constant)	11 6 g	271·0	S_3 160—165° (gradually rising above 180°)	1 05 g	290 0
S_2 152— 155° (rose to 180°C)	2·1 g.	272·1	S_4 Residue	1 2 g	

As will be seen about 85·6% came over in the first two fractions. The saponification equivalent of S_1 and S_2 (271 and 272 1 respectively) correspond to that of methyl palmitate. The acid was regenerated from S_1 and S_2 mixed together and recrystallised from alcohol, m. p. 62° (anilide, m p. 87°). Anilide of palmitic acid melts at 87·5°. Hence the acid is palmitic and fractions S_1 and S_2 contain palmitic ester. Fraction S_3 had a saponification equivalent 290, which is nearly equal to that of methyl stearate (297). It melted between 35° and 36·5°. The acid was generated and found to melt at 70° (m. p. of steric acid, 72°). Hence the acid is stearic and S_3 contains mainly stearic ester. Calculations on the basis of saponification equivalents give palmitic acid (20·84%) stearic acid (2·16%) in the original oil.

The unsaponifiable portion yields a needle-shaped crystalline sterol which is under examination.

The seeds after extraction of the oil have been successively extracted with other solvents and we have been able to get crystalline products from the ethyl acetate and alcoholic extracts ; these are also under examination.

COMPONENT FATTY ACIDS OF OIL OF *CITRULLUS·VULGARIS*, SCHRAD (WATER-MELON) SEED

By D. R. DHINGRA AND ANIL KUMAR BISWAS

Component fatty acids of *Citrullus Vulgaris*, Schrad consist mainly of oleic and linoleic acids which are characteristic of *Cucurbitaceae* : caprylic (0·2%), capric (1·1%), lauric (0 8%), myristic (0 2%), palmitic (7·6%), stearic (6·1%), oleic (35 3%), linoleic (48·7%)   Unsaponifiable matter in the oil is 0·2%

Citrullus Vulgaris, Schrad belongs to the N.O. *Cucurbitaceae* and is an annual creeper, grown abundantly in many parts of India. It is known as water-melon in English; Tarbuz or Tarmuz in Hindustani; and Hindwana in Punjabi. Its fruit is delicious and is full of watery juice. Seeds are aphrodisiac, tonic to brain, diuretic and strengthening.

No detailed study of the Indian melon-seed oil has been made in the past. Its oil is used for adulteration of the more expensive almond oil. We have found that the oil from water-melon kernels has pleasant smell and is tasteful. There seems to be no reason why it should not be used as a substitute for almond oil. Water-melon oil is reputed in Indian medicine to be nutritive and cooling on its application to head. Wehmer in his book 'Pflanzenstoffe' (1931 Edition) has mentioned that water-melon seed kernels are fairly rich in nitrogenous substances and phosphates and hence they can form a fairly good substitute for the more expensive almond kernels.

Water-melon oil is a semi-drying oil and its component fatty acids are caprylic (0·2%), capric (1·1%), lauric (0·8%), myristic (0·2%), palmitic (7·6%), stearic (6·1%), oleic (35·3%), and linoleic (48·7%). Unsaponifiable matter present in it is 0·2%. Power and Salway (*J. Amer. Chem. Soc.*, 1910, **32**, 360) reported the component fatty acids of American water-melon (*Cucurbita Citrullus*) to be linoleic (45%), oleic (25%), palmitic and stearic (30%). The composition is different from that of the present oil and it seems that the American species was of different type. Fatty acid-composition of the water-melon seed oil given by Pierserts (*Bull. Soc., Pharmacol*, 1917, **24**, 204) is 2·5% lauric, 12·6% palmitic, 15·2% stearic, 43·4% oleic and 26·3% linoleic which is different from that of the present oil. Water-melon seeds examined by Pierserts seem to be of a different species. Nolte and Loesecke (*J. Amer. Chem. Soc.*, 1939, **61**, 889) examined seed oil of Cuban Queen variety of water-melon and gave fatty acid composition as follows : oleic (13·03%) linoleic (68·38%), palmitic (8·84%), stearic (5·64%), archidic (0·72). They did not fractionate liquid acids and hence could not find out lower saturated acids which get dissolved in alcohol-soluble portion during lead-salt separation of mixed acids   We wish to emphasise that fractionation of liquid unsaturated acid portion is also very necessary to get correct composition. Percentage of saturated acids seems to agree somewhat but that of unsaturated acids differs from that of the Indian oil. However, total percentages of unsaturated acids agree with each other and high percentage of these acids is characteristic of *Cucurbitaceae*, as pointed out by Hilditch (*Allgem, Oel-u Fett. Ztg.*, 1930, **27**, 184, 219, 255). It has been found that the fat from different species

of these seeds show some differences in composition, as in *Citrullus Pepo* (Reibsomer and Mesty, *J. Amer. Chem. Soc.*, 1934, **56**, 1784) which has 5˙9% palmitic, 7˙1% stearic, 40˙9% oleic and 46˙1% linoleic acids. Lower fatty acids (caprylic and capric) are also characteristic of the Indian water-melon seed fat, like that of melon seed fat.

Preliminary study of the glyceride structure reveals the absence of fully saturated glycerides and the presence of only 0˙9% trilinolein in spite of the presence of 48˙7% linoleic acids in the mixed acids. Thus it is clear that fatty acids are evenly distributed in the glycerides and it is in accordance with the theory of "even distribution of fatty acids in the seeds oil" of Hilditch (Collin and Hilditch, *Biochem. J.*, 1929, **23**, 1273). From the association ratio of saturated to unsaturated acids (1 : 4˙68) also, it is clear that fully saturated glycerides would not be present in the oil.

EXPERIMENTAL

Citrullus vulganis, Schrad or water-melon seeds of red shell and not of black shell were obtained from N. W. Punjab (India) and the oil was pressed out of their kernels by cold pressing in a small press. Sediment in the oil was removed by filtration. The oil obtained is liquid at ordinary room temperature and possesses pleasant smell, agreeable taste and pale yellow colour. General characteristics of the oil along with those of West African and Cuban oils are given in Table I.

TABLE I

Particulars	Citrullus Vulgaris (Water-melon) kernel oil, Indian	C Vulgaris (Cuban) Nolte and Loesecke (loc cit)	C Vulgaris (West African, Grimme Chem Zentıl., 1911, il, 1742)
Yield of oil	45˙5% from kernels	26˙52% from seeds	15˙33% from seeds
Specific gravity	——	0˙9197	0 9143
Saponification value	196˙3	197˙4	198˙2
do eqnivalent	285 4	283 6	282˙5
Iodine value	124˙2	133 8	123˙7
Acid value	5˙2	0˙42	——
Refractive index n_D^{20}	——	1 4669	1˙4728
Unsaponifiable matter	0 3%	——	1˙34%

Examination of the Fatty Acids.—The oil (250 g.) was saponified with alcoholic potassium hydroxide and mixed acids were obtained by the usual method. Acids were separated into "liquid" and "solid" fractions by the lead-salt alcohol method of separation and each fraction was converted into methyl esters which were separately fractionated under high vacuum of about 1 mm pressure. Each fraction was analysed and acids present in esters were identified (data in Table II.)

TABLE II

Mixed fatty acids :

Saponification value 268·0 and iodine value 120·8
Corresponding methyl esters

"Liquid" (L) acids 85 4%

| Saponification equivalent 281·1 (calculated 282·0) | Iodine value. 134·0 (calculated 133·0) |

"Solid" (S) acids 14·6%

282·8   5·1

TABLE III

(1) Methyl ester of "Liquid" (L) acids.

No.	g	B p.	S.E	I V	No	g.	B p.	S.E.	I.V.
					L1a	6·19	163-164	276 7	118·1
					L1b	6·57	164-168	282·7	132·2
L1	21·29	178·182	280·1	127·8	L1c	2 97	168-169	281·3	136·0
					L1d	0·40	Residue	280·9	136·7
L2	13·28	182-183	280·5	135·3					
L3	10 01	183-184	280 2	136·8					
L4	3·44	184	282 8	136·8					
L5	8·36	Residue	291 5	137 0					
,,	Acids	Ex-N-S	282 0	142·1					
,,	Esters	Ex-N-S	296 0	135 4					

(ii) Methyl esters of "Solid" (S) acids.

No	g	B p	S E.,	I.V.
S1	3 92	160-164	277·3	3·45
S2	4 53	164-171	279·0	3·41
S3	6 23	171-175	283 8	5 96
S4	2·34	175	296·1	8·40

TABLE IV

Fatty acids (calculated).

Acids	Solid Acids 14·6%	Liquid Acids 85·4%	% Total fatty acids Including N-S	Excluding N-S	Mols Ex N-S
Caprylic	—	0·2	0 2	0·2	0·4
Capric	—	1·1	1·1	1·1	1·7
Lauric	—	0 8	0 8	0·8	1·0
Myristic	—	0·2	0·2	0·2	0·3
Palmitic	7·6	—	7 6	7·6	8·3
Stearic	6·1	—	6 1	6·1	5·9
Oleic	0·9	34·3	35·2	35·3	34 5
Linoleic	—	48·6	48·6	48·7	47·9
Unsaponifiable matter	—	0 2	0·2	—	—

Association ratio of saturated to unsaturated fatty acid mols is 1 : 4·68.

Identification of the Acids.—L1a and L5 fractions were hydrolysed with alcoholic potassium hydroxide and oxidised with potassium parmanganate in ice-cold aqueous alkaline solution. Dihydroxystearic acid (m.p. 129°) and tetrahydroxystearic acid (m.p. 174°) were obtained from both of the fractions showing the presence of oleic and linoleic acids respectively.

S$_1$.—Dihydroxy stearic acid was obtained by oxidation of oleic acid and palmitic acid (m.p. 63°) and stearic acid (m.p. 69°) were also identified.

S$_4$.—The same acids as in S$_1$ were obtained.

Glyceride structure.—Neutral oil (100 g.) was dissolved in acetone and cooled to —5° for 4 days. No fully saturated glycerides separated. It was further oxidised by potassium permanganate but no fully saturated glycerides could be isolated.

Bromination.—Neutral oil (100 g) was brominated in petroleum ether and the brominated products were separated into several fractions by suitable solvents. Alcohol-insoluble -fractions showing the presence of trilinolein did not exceed 0·9%. Further investigation of the other glycerides present in the oil is in progress.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF DELHI.

COMPONENT FATTY ACIDS OF MELON (*CUCUMIS MELO*, LINN). SEED OIL

By D. R. DHINGRA and PREM NARAIN

Component fatty acids of melon seed kernels consist of caproic (1·0%), caprylic (2·0%), myristic (1·1%) palmitic (7·3%), stearic (0·2%), oleic (43·1%) and linoleic acids (45·1%) Unsaponifiable matter in the oil is 0·9%.

Fully saturated glycerides are absent in the oil Trilinolein does not exceed 1%, although 45·2% of linoleic acid are present in the mixed fatty acids. Thus acids are evenly distributed in the glycerides.

Kernels contain 40% oil, 22·7% proteins and 0·75% phosphates as P_2O_5 and can be used as a fairly good substitute for the more expensive almond seeds, as article of nutritive food.

The oil of seeds of melon or sweet melon (*Cucumis melo*, Linn), known in Hindustani Kharbuza, in Bengali- Khurmuj, has been examined for the component fatty acids. The plant is an annual creeper and belongs to N. O. *Cucurbitaceae*. Melon fruit is grown abundantly all over India, and the seeds form a by-product. The seed kernels are used for edible purposes as substitute for more expensive nuts like almond kernels and pistachio kernels The seeds are nutritive and are also used in India medicinally as lachrymatory, diuretic, for treatment of gonorrhoea and for curing painful discharge of urine.

The seed kernels contain a high percentage of oil (40%) and also contain a fairly high proportion of proteins (22·7%) and some phosphates (0·75% as P_2O_5). The present price of the melon kernels is about 33% of the almond kernels and considering their high nutritive value, they should form a fairly good substitute for the more expensive almonds and pistachio kernels, used as articles of rich and nourishing food. The oil obtained is also of a very fragrant smell, pleasant taste and can replace the more expensive almond oil valued for its high medicinal value. Melon seed oil is a semi-drying oil as seen by the data of the component fatty acids (oleic, 43·2% : linoleic, 45·2% ; caproic, 1·0% ; caprylic, 2·0% ; myristic 1·1% , palmitic 7·3% ; stearic 0·2%). Unsaponifiable matter present in the oil is 0·9%. The composition of acids in the oil is in concordance with that of most of the other members of *Cucurbitaceae*, as shown by the generalisation of Hilditch (*Allgems—Oel-u. Fett- Ztg.*, 1930, 27, 184, 219, 255). The composition of oil of melon seed from California given by Baughman and Jamieson (*J. Amer. Chem. Soc.*, 1920, 42, 152), given in Table IV, is somewhat different from that of the present oil, but total of unsaturated acids is almost similar. High percentege of oleic and linoleic acids is characteristic of this botanical family. Differences are due to a different origin of the seeds and also perhaps due to different species of *Cucumis melo*.

It has been observed in the case of several seeds that if the outer cover of the kernels is hard and tenacious, the seed fat is rich in saturated fatty acids but if otherwise, unsaturated acids predominate as component acids of glycerides as also shown by the present melon seed fat. Fully saturated glycerides are completely absent as expected from the comparatively low percentage (11·6%) of saturated acids. Moreover, although 45·2% linoleic acid is present in the mixed acids, yet trilinolein does not exceed 1·0%.

Thus, there is even distribution of fatty acids in the glycerides and it supports the theory of even distribution of Hilditch (Collin and Hilditch, *Biochem. J.*, 1929, **23**, 1273) in seed fats.

EXPERIMENTAL

The oil was extracted out of soft seed kernels from Punjab (India) seeds in a small press and it was clarified by filtration. The content of the oil in the kernels is 40% by ether extraction. The oil is bright pale-yellow in colour and possesses a pleasant smell and agreeable taste.

Some of the general characteristics of the oil, along with those of a few similar varieties are given in Table I.

TABLE I

Particulars	Cucumis Melo Linn (Indian)	Cucumis Melo L (African) Fendler*	Cucumis Sativus (Indian) Hooper†	Melon seed oil (S. Russian) Lidoff. ‡
Yield of oil by extraction	40·0%	...	...	29 4%
Specific gravity	...	...	0·923-0·924	0·9276
Saponification value	207·4	193·3	195·2 196 9	190·5
Saponification equivalent	270·0	289·7	284·7-286·8	293·9
Acid Value	0 9	...	11 5	1 37
Iodine value	117 1	101·5	117 7-118·5	133·3
Unsaponifiable matter	0·79%	...	...	...

* Fendler, *Bull, Imp. Inst.* 1913, 56

† Hooper, Annual Report. Indian Museum, 1907-1908, 13

‡ J. Lewkowitsch, Chemical Technology and Analysis of Oils, Fats and Waxes., Vol. II, (1922), p. 171.

Iodine value of the present oil is same as that of the melon seed oil examined by Hooper (*loc. cit.*) but saponification value is different. Low saponification value of the oil under examination is due to the presence of lower fatty acids. African and Russian oils are different from the Indian oil.

Examination of the Component Fatty Acids.—250 G. of the fat were saponified and the mixed acids separated into solid and liquid acids by lead salt-alcohol method. Each group of the acids was separately esterified to methyl esters and esters were fractionated under high vacuum of about 1 mm. Each fraction was separately examined and individual acids present were identified (Tables II and III)

TABLE II

Mixed fatty acids :—Saponification equivalent, 266 9, (calculated 267·4) ;
Iodine value, 120 6 (calculated 119·6).

		Corresponding Methyl esters.	
		Sap. equiv.	I.V.
Solid acids (S)	8·8%	267·0	1·80
Liquid Acids (L)	91 2%	267 4	124·2

TABLE III

(i) *Methyl esters of "Liquid" (L) acids.*

No.	Wt	B.p.	S.E.	I.V	No	Wt.	B.p.	S.E.	I V
L₁	25 40 g.	148-177	259·1	118 4	L₁ₐ	4·49	165-180	245·8	102·2
L₂	8·53	174-179	264·2	127·0	L₁ᵦ	6·10	181-182	256·1	112·0
L₃	8 44	181-183	168·5	127·8	L₁ᵪ	6·30	182	266·1	128 7
L₄	6 91	183-190	270·9	129·5	L₁ₔ	3·10	Residue	272 9	130 2
L₅	4 78	195-208	276·1	130·4					
L₆	15·20	Residue	281 0	132·9					
,,	Acids-ex N.S (Found)		276 4	135·8					
,,	Esters-ex N. S								
	(Calculated)		290 4	129·2					

(ii) *Methyl esters of "solid" (S) acids*

No.	Wt	B.p.	S.E.	I.V.
S₁	4 99 g.	160-167	262·3	1·40
S₂	3·54	170-176	265 9	1·54
S₃	3·80	178-188	267·4	2·10
S₄	4·20	Residue	273 3	2·30

Identification of Acids.—Some of the ester fractions were hydrolysed and aqueous potassium salts of fatty acids were oxidised with alkaline permanganate solution. Unsaturated acids resulted in the production of hydroxy acids which were separated from the saturated acids by suitable solvents and were subjected to fractional crystallisation.

L₁ₐ :—Dihydroxystearic acid (m. p. 129°) and tetrahydroxystearic acid (m. p. 174°) were isolated, showing the presence of $\Delta^{9 \cdot 10}$—oleic acid and $\Delta^{0 : 10 : 12 : 18}$ linoleic acid respectively.

L₂ :—The same acids as mentioned in L₁ₐ fraction were confirmed.

S₁ :—Myristic acid (m. p. 54°) and palmitic acid (m. p. 62°) were identified.

S₄ :—The main acid in this fraction was palmitic acid (m. p. 62·5°) and stearic acid (m. p. 70°) was also separated.

From the above data, component fatty acids and unsaponifiable matter present in the oil were calculated and Table IV gives the percentage composition of these.

TABLE IV

Acids	"Solid" acids 8·8%	"Liquid" acids 91·2%	Percentage of total fatty acids Including N-S	Excluding N-S	Mols Ex N-S	Melon seed Baughamann & Jamieson (*loc. cit.*)
Caproic	...	1·0	1·0	1·0	2·3	...
Caprylic	...	2 0	2 0	2·0	3·7	...
Myristic	1·2	.	1 2	1 2	1·3	0·3
Palmitic	7·2	...	7·2	7 3	7·6	10·3
Stearic	0·2	...	0·2	0·2	0·2	4·6
Oleic	0·2	42·5	42·7	43·1	41·3	27·5
Linoleic	...	44 8	44·8	45·2	43·6	57·3
Unsaponifiable matter	...	0·9	0·9	...	...	...

Association ratio of mole of satutated to unsaturated acids is $1 : 5.62$.

Glyceride Structure.—Oil (100 g.) was dissolved in acetone and kept at—5° for some days in a frigidaire. No solid separated, showing thereby the absence of fully saturated glycerides.

Bromination.—The oil (100 g.) was dissolved in petroleum ether (40-60°) and brominated at −5°. Brominated glycerides were fractionally separated into several fractions by absolute alcohol, alcohol and acetone, and acetone etc. Alcohol-insoluble fraction corresponding to trilinolein was not more than 1% of the total.

Other fractions are being studied further.

•*Seed Analysis.*

Kernels of the seed were extracted with ether and oil-free seed-cake was analysed for nitrogen by Kjeldahl's method and also for phosphorus. Proteins (22.7%) and phosphates (0.75% as P_2O_5) were thus found to be present in the kernels.

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COMPONENT FATTY ACIDS OF KÁHU (*LACTUCA SCARIOLA*, LINN) SEED OIL

BY D. R. DHINGRA AND KRISHAN PERSHAD

The seed oil of *Lactuca scariolia*, Linn contains the following component fatty acids : caproic (2·1%), palmitic (1·8%), stearic (1·3%), arachidic (0·1%) oleic (36·5%) and linoleic (55·1%). It contains 0·6% of trilinolein and thus in spite of of high percentage of linoleic acid there is an even distribution of fatty acids in the glycerides

The seeds also contain a high percentage (3·1% on oil) of unsaponifiable matter. Arsenic in mere traces, iron, phosphorus, sodium, potassium, calcium, aluminium, nitrate, chloride have also been found in the seeds.

Lactuca scariola, Linn belongs to the N. O. *Compositæ*, and the plant is widely grown in Western Himalayas. It is known as lettuce in English and Kāhu or Kahoo in Hindustani. The plant is 1-3 ft. in height generally, but sometimes it is 6 ft high. The seeds are oblong, about 1 cm. long and 1-2 mm. wide in the centre and resembles to some extent those of Caraway seeds. The seeds are used in India for relieving cough, asthma, pertussis and insomnia etc. The oil of the seeds is reputed to be beneficial for relieving melancholia, headache, inflammations and epilepsy and has hypnotic and antipyretic properties. The oil is also used as a cure for falling hair.

The seeds contain mere traces of arsenic and a fairly good amount of iron, phosphorus. On account of high content (35·5%) of oil of great medicinal value in the seeds which are available in plenty in India, the oil should form a good and cheap substitute for the more expensive almond oil. Seed is grown in crops and has not been commercially utilised so far.

The Kahu oil is semi-drying in nature and has a high percentage of unsaturated acids : oleic (36·5%), linoleic (55·1%) saturated acids (5·3%), caproic (2·1%), palmitic (1·8%), stearic and (1·3%) arachidic (0·1%) and high percentage of unsaponifiable matter (3·1%). This conforms to the generalisation of Hilditch that the seed fats of *Compositae* family contain a fairly high percentage of unsaturated acids,

In spite of the high content of linoleic acid (55·1%) in the mixed fatty acids of the oil, trilinolein determined does not exceed 0·6% in the glycerides. Moreover, fully saturated glycerides are absent in the oil. This gives a support to the even distribution theory of Hilditch (Colli and Hilditch, *Biochem. J.*, 1929, 23, 1273) in seed oils namely (*a*) that in the seed-fats the component fatty acids are evenly distributed throughout the glyceride molecules, and (*b*) that fully saturated glycerides are produced in very small quantity in kernel fats, except when the amount of saturated fatty acids present is greater than that necessary to link with unsaturated fatty acids (in the form of mixed glycerides) in the molar ratio of about 1·3-1·4 of saturated to 1·0 of unsaturated fatty acids.

EXPERIMENTAL

The oil was obtained by cold pressing of the seeds in a small press and clarified by filtration. The oil is of a greenish yellow colour and possesses a pleasant smell and

somewhat sharp taste.   It can be used for medicinal purposes and also for edible purposes after refining.

No data about the oil except a few characteristics of Egyptian oils are available and these along with those of the Indian oil are given in Table I.

TABLE I

General characteristics of Kahu oil.

Particulars	*Lectuca scariola* (Indian).	*L. Scariola oleifeia* (Egyptian) *
% oil in seeds	35'5	36'1
Specific gravity	—	0'9283
Refractive index	1'4879 at 25°	1 4682
Sap. Equiv.	290 6	293'0
Iodine value	123 5	127'6
Acid value	8'5	10 6
Unsaponifiable matter	3 0%	—

Composition of Fatty acids of Kahu Fat.—The oil (300 g.) was saponified with alcoholic potassium hydroxide and mixed acids, liberated, had saponification equivalent 280'5 and Iodine value 132'5. These acids were subjected to lead salt separation in alcoholic solution and resolved into solid, liquid and acids, which were separately esterified to methyl esters.   The esters were fractionally distilled under high vacuum of 1 mm pressure. Each fraction was analysed and the acids in these were identified by suitable methods (Tables II and III).

TABLE II

Acids	%	Corresponding methyl esters Sapon. equiv	Iodine value.
" Solid " (S)	3'33	282'9	3'7
" Liquid " (L)	96 67	286 0.	132 8

TABLE III

(i) Methyl esters of liquid (L) and Solid Acids (S).

No.	Wt.	B.p.	S.E.	I.V	No	Wt.	B.p	S E.	I.V
		Liquid acid					Liquid acid		
L_1	31'68 g.	154-170	274 3	130 5	$L_1 (a)$	6 57 g	165-179	269 9	128 0
L_2	6'27	170-172	275'0	131'5	$L_1 (b)$	8 20	176-180	274'2	130 6
L_3	8'73	172-176	278'3	132 9	$L_1 (c)$	8 54	179-184	276 9	131'9
L_4	8'09	176-177	290'0	134'9	$L_1 (d)$	1 50	Residue	277'0	134'5
L_5	8'85	176-178	318'5	136 8			Solid acids		
L_6	7'38	Residue	325'0	138'2	S_1	2 58	169 181	272'0	3 51
,,	Acids	ex N-S (Found)	319'1	141'9	S_2	2 29	181-193	280'5	3'40
,,	Esters	ex N-S (Calculated)	333'1	135'9	S_3	2'01	Residue	301'2	4'20

* E. Griffiths—Jones.   Rep. Pub. Health Laboratories, 1918, 1, and Bull. Imp. Inst., 1919, 37.

Identification of Acids.—The individual ester fractions mentioned below were hydrolysed by alcoholic potash and then potassium salts were oxidised with ice-cold potassium permanganate solution in dilute aqueous alkaline solution. Saturated fatty acids were separated from hydroxy fatty acids (produced by oxidation of ethylénic acids) by hot petroleum ether. The saturated acids were crystallised from alcohol and hydroxy acid from ethyl acetate and water.

L_1 (a) :—Dihydroxystearic acid of m.p. 129° and tetrahydroxystearic acid of m.p. 169° were identified, showing the presence of $\Delta^{9 \cdot 10}$- oleic acid and $\Delta^{9:10, 12:13}$. linoleic acid respectively.

L_6—The same acids as mentioned in L_1 (a) were identified, *e.g.*, dihydroxystearic acid (m.p. 129'5°) and tetrahydroxystearic acid (m.p. 170°).

S_1—Palmitic acid (m.p. 62°) was separated.

S_3—Stearic acid of m.p. 70° was identified.

Final data of the component acids from various ester fractions are summarised in Table IV.

TABLE IV

Acids.	Solid acids 3'33%·	Liquid acids 96'67%	Total percentage of fatty acids including N-S.	excluding Unsap. Mat.	Mols. ex N-S
Caproic	—	2'14	2'1	2'2	5'2
Palmitic	1'82	—	1'8	1'9	2'0
Stearic	1'24	—	1'3	1'3	1'2
Arachidic	0'13	—	0'1	0'1	0'1
Oleic	0'14	36'32	36'5	37'6	36'3
Linoleic	—	55'07	55'1	56'9	55'2
Unsaponifiable matter	—	3'14	3'1	—	—

Association ratio of saturated to unsaturated acids mols is 1'0 : 10'73.

Component Glycerides of Kahu Oil.—Neutral oil (100 g.) was brominated in petroleum ether solution at −5° and the brominated product was subjected to fractional separation into different fractions by absolute alcohol, acetone-alcohol and acetone. Alcohol-insoluble portion corresponded to 0'6% of trilinolein. Further work on glyceride structure is in progress. On account of very low percentage of saturated acids in the oil, no fully-saturated glycerides could be isolated.

Examination of Seeds.—Seeds were carefully heated in a crucible and the ash obtained was qualitatively analysed. It showed the presence of iron, sodium, potassium, phosphorus, aluminium, calcium, nitrates, chlorides and mere traces of arsenic.

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A NOTE ON THE CLASSIFICATION OF ELEMENTS

By Pares Chandra Banerjee

Since the time of Mendeleeff, the "Periodic Table" has, no doubt, undergone many changes with modifications here and there, but some of its defects still remain to be solved. For example, the position of the rare-earths in the periodic table is a matter of some complexity. Another example is the position of hydrogen. It has not yet been possible to assign any definite position to these elements.

With a view to removing the difficulties, without sacrificing the merits of the existing tables, the following classification based on atomic number and valency electrons is suggested. This mode of representation seems to be simpler and clearer and it is believed, will be more easily intelligible to students. The elements are arranged by plotting their atomic numbers as ordinates and valency electrons as abscissa. By valency electrons is understood, the number of electrons in the highest quantum group of the element together with those in the d-level of the preceeding group, so long as the latter (*i.e.* d-level) is incomplete. The total number of such valency electrons in any element varies from zero to ten but is never greater than ten. When the d-level becomes complete, all the valency electrons are supposed to lie in the outermost layer of the element, Thus calcium has two valency electrons, scandium has three, nickel ten, copper one and so on.

GROUPS

Period		o	I	II	III	IV	V	VI	VII	VIII	IX	X
		A	B A	B A	B A	B A	B A	B A	B A	B A	B A	B A	B

Figure: chart plotting Atomic Number (ordinate) against Valency electron (abscissa), with periods labelled on the left: 4. LONG P., 3 LONG P., 2 LONG P., 1 LONG P., 2 SH. P., 1 SH. P. Element symbols plotted include: Nt, Ra, Ac, Th, Pa, U; Au, Hg, Tl, Pb, Bi, Po; Lu, Hf, Ta, W, Re, Os, Ir, Pt; Xe, Cs, Ba, La; Ag, Cd, In, Sn, Sb, Te, I; Kr, Rb, Sr, Y, Zr, Nb, Mo, Ma, Ru, Rh, Pd; Cu, Zn, Ga, Ge, As, Se, Br; A, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni; Ne, Na, Mg, Al, Si, P, S, Cl; He, Li, Be, B, C, N, O, F; n, H. Atomic number axis marked at 10, 20, 30, 40, 50, 60, 70, 80, 90. Valency electron axis marked o, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10.

Valency electron.

Thus, starting with, helium. the elements have been arranged in two short periods, followed by four long periods, the last one being incomplete. Hydrogen is placed along with neutron in series I before the first short period. The elements are also divided according to their valency electrons into eleven vertical groups beginning from o to 10 as shown in the table.

The main characteristics which distinguish the present table from the older ones are that (i) the rare-earths having the same number of valency electrons (one in 5-d and two in 6-s) are all placed in group III; (ii) hydrogen having a single valency electron is placed in group I; (iii) the eighth group instead of containing all the nine elements of the three triads contains only one member from each set, the others being placed in groups IX and X. The position of hydrogen in group I explains its similarities not only with the alkali metals but also with the halogens, because, by the gain of an electron, it attains the stable configuration of an inert gas, helium, just as the halogens do.

The inert gases (except He) which have eight electrons in the outermost layer and the full number of electrons in the d-level of the preceeding group, should be placed in group VIII, according to the above classification. But considering that these elements have completed the octet and that a new electron if added, would find its way into the next higher quantum group and give rise to an element with one valency electron, the inert gases may also be regarded as having zero number of electrons in the highest and eight electrons in the layer next the higest quantum group. Thus, argon with eight electrons in the M-shell (2 in s, 6 in p, and o in d-level) and with no electrons in the N-shell may be said to have zero number of electrons in the highest quantum group. In this way, all the inert gases may be regarded as having no electron either in the highest quantum group or in the d-level of the preceeding group. The number of valency electrons of these elements is therefore zero and they are placed in the zero group instead of group VIII.

Another characteristic feature of the present classification is that all the non-transition elements, whose valency electrons lie exclusively in the highest quantum group belong to sub-group A; while the rest, which are all transition elements and whose (except Cu, Ag, Au, Zn, Cd and Hg) valency electrons are distributed into the last two quantum groups belong to sub-group B. Thus every group is divided into two sub-groups A and B; A containing the non-transition elements placed to the left hand side of each vertical line and B containing the rest which are all transition elements, placed to the right as shown in the table*. In the list of transition elements, mentioned above, have been included all the elements (viz., Sc-Zn; Y-Cd; La-Hg and Ac-U) which are formed by the gradual entry of the additional electrons, consequent on increasing atomic number, into the inner layers of the electron shell, instead of the outer layer only being built up.

My best thanks are due to Prof. P. Rây, for some of his useful suggestions.

*This is, however, contrary to the usual arrangement—Ed.
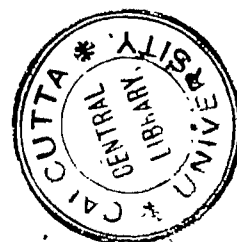
SYNTHESIS OF DININIC ACID*

BY BIDYUT KAMAL BHATTACHARYYA

The sodio derivative of ethyl 2-methyl-2 : 3-dicyano-propane-3-carboxylate on treatment with β-ethoxy ethyl iodide furnishes ethyl 2-methyl-2 : 3-dicyano-pentane-5-ethoxy-3-carboxylate which on hydrolysis gives dininic acid.

Kir'yalov (*J. Gen. Chem.* U.S.S.R., 1938, **8**, 740 ; 1939, **9**, 401, 432) has obtained a lactonic acid (dininic acid) by the degradation of biglandulinic acid isolated from the juice of *Euphorbia Biglandulosa.* The author has conclusively proved from analytical data that dininic acid should possess the structure (I)

$$H_2C \underset{\underset{\displaystyle O}{H_2C} \diagdown CO}{\overset{\displaystyle CH}{\rule{0pt}{0pt}}} \quad C \overset{\displaystyle CH_3}{\underset{\displaystyle CO_2H}{\rule{0pt}{0pt}}} CH_3$$
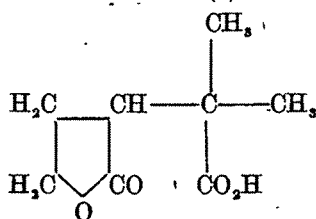
(I)

In the following lines has been described a method by which the synthetical confirmation of the above structure has been achieved.

Acetone cyanohydrin has been condensed with ethyl sodio-cyanoacetate in alcoholic solution and then β-ethoxy ethyl iodide is allowed to react on the resulting compound *in situ* according to the method of Thorpe and Higson (*J. Chem. Soc.,* 1906, **89**, 1455) when (II) is obtained. The pentane derivative (II) is hydrolysed by heating with concentrated hydrochloric acid in acetic acid solution in a sealed tube, when the elimination of carbon dioxide and lactonisation occur simultaneously to yield (I). It is crystallised from petroleum ether and chloroform, m.p. 129-31.5°. Dininic acid, obtained by the degradation of the natural product, melts at 129-31°.

$$\underset{\underset{\displaystyle CN}{CH_3}}{\overset{\displaystyle CH_3}{\underset{\displaystyle\rule{0pt}{0pt}}{C}}} \text{—CNa—CO}_2C_2H_5 + I.CH_2.CH_2.OC_2H_5$$

$$CH_2 \underset{\underset{\displaystyle OC_2H_5}{CH_2}}{\overset{\displaystyle CO_2C_2H_5}{\underset{\displaystyle CN}{C}}} C\diagup^{CH_3}_{\diagdown CH_3} \underset{CN}{\rule{0pt}{0pt}}$$

(II)
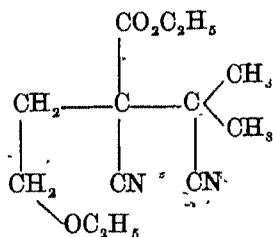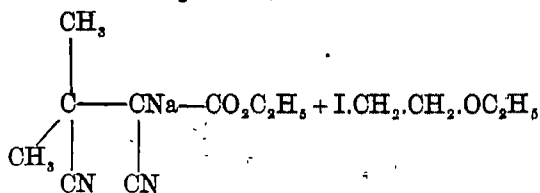
EXPERIMENTAL

Ethyl 2-Methyl-2 : 3-dicyano-pentane-5-ethoxy-3-carboxylate (II).—β-Ethoxy ethyl iodide (66 g.) was added to sodio derivative of ethyl 2-methyl-2 : 3-dicyano-propane-3-carboxylate prepared from acetone cyanohydrin (28 g. in 20 c.c. alcohol) and ethyl sodio-cyanoacetate (sodium, 7.1g., ethyl cyanoacetate, 36.6 g. and alcohol, 114 c.c.) according to Thorpe and Higson (*loc. cit.*) and the reaction mixture was refluxed for 36 hours. It was next diluted with water, extracted with benzene and distilled, b.p. 152-4°/6.5 mm., yield 14 g. (Found : C. 61.6 ; H, 8.06. $C_{13}H_{20}O_3N_2$ requires C, 61.9 ; H, 7.93 per cent).

γ-Lactone of 2-Methylpentane-5-ol-2 : 3-dicarboxylic acid (I).—The above condensation product (5.5 g.) was heated in a sealed tube with a mixture of hydrochloric (d 1.19, 20 c.c.) and acetic (16 c.c.) acids at 175-85° for 10 hours. The reaction mixture was diluted with a small quantity of water and thoroughly extracted with ether. The ether was driven off and the residue solidified on keeping under vacuum. It was first crystallised from acetone in which it was readily soluble and then from a mixture of petroleum ether (b.p. 40-60°) and chloroform. The acid, on heating, shrinks at 129° and melts at 130-31.5°. (Found : C, 56.05 ; H, 6.5. $C_8H_{12}O_4$ requires C, 55.81 ; H, 6.97 per cent).

The above lactonic acid (1.4551 g.) furnished a cinchonidine salt when treated with cinchonidine (2.4872 g.) in aqueous (6 c.c.) methanol (20 c.c.) and allowed to stand for several hours. The salt was crystallised several times from dilute methanol, m.p. 183°. (Found ; C, 69.38 ; H, 7.32. $C_8H_{12}O_4$, $C_{19}H_{22}ON_2$ requires C, 69.3 ; H, 7.25 per cent).

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ORGANOMETALLIC COMPOUNDS OF THE ALLYL RADICAL. PART II*
TIN TETRA ALLYL AND ITS DERIVATIVES

BY K. V. VIJAYARAGHAVAN

Tin tetra-allyl has been isolated by the action of allyl magnesium bromide on stannic halides. By the action of bromine on the substance, tin triallyl bromide and by the action of stannic bromide, tin diallyl dibromide have been prepared. A pyridine derivative of the latter is also described.

Though a large number of organic compounds of tin are described in the literature (Goddard and Goddard, "Text Books of Inorganic Chemistry" Vol. XI, Organo-Metallic Compounds : p. 300 and *et. seq.*) the only reference to an organic compound of tin where the allyl radical is involved is to allyl stannonic acid, CH_2 : $CH.CH_2$. $Sn{\nwarrow}^O_{OH}$ (Lesbre and Glotz, *Compt. rend.*, 1934, **198**, 1426) which corresponds to CH_2 : $CH.CH_2.C{\nwarrow}^O_{OH}$.

Tin tetra-allyl has been prepared by the action of allyl magnesium bromide on stannic chloride (*cf.* Pope and Peachey, *Proc. Chem. Soc.*, 1903, **19**, 290 ; Pfeiffer and Schnurmann, *Ber.*, 1904, **37**, 320).

$$4C_3H_5MgBr + SnCl_4 \longrightarrow Sn(C_3H_5)_4 + 2MgBr_2 + 2MgCl_2.$$
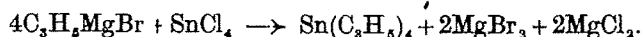
The weight of magnesium taken is twice the theoretical amount for the allyl bromide in order to prevent the Wurtz reaction (*cf.* Gilman and Mac-Glumphy, *Bull. Soc. chim.*, 1928, *iv*, **43**, 1322) taking place.

$$C_3H_5MgBr + C_5H_5Br \longrightarrow C_6H_{10} + MgBr_2$$
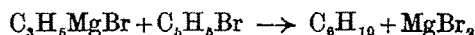
The amount of allyl magnesium bromide used is twice the theoretical quantity to prevent the formation of any tin triallyl halide. The use of stannic bromide gave a lower yield of tin tetrallyl.

Tin tetra-alkyls are acted upon by the halogens, especially by bromine and iodine, the halogens displacing the alkyl radicals and forming tin trialkyl halides or tin dialkyl dihalides depending upon the amount of halogen used (Krause and Sessions, *J. Amer. Chem. Soc.*, 1925, **47**, 2361 ; Goddard and Goddard, *loc. cit.*). Tin tetra-allyl decolourises solutions of bromine in carbon tetrachloride and carbon disulphide. Even when theoretical quantities for the formation of tin triallyl bromide,

$$(C_3H_5)_4Sn + Br_2 \longrightarrow (C_3H_5)_3SnBr + C_3H_5Br$$
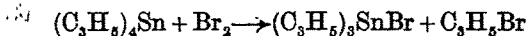
are used, traces of tin diallyl dibromide are also formed, and the separation of the two has not been possible. The use of pyridine as the solvent in the bromination of tin tetra-allyl (*cf.* Krause, *Ber.*, 1918, **51**, 912) does not improve the purity of the product.

Kozeschow (*Ber.*, 1933, **66, B,** 1661) has studied the action of stannic halides on tin tetra-alkyls in detail and has prepared tin alkyl halides by this method.

$$3SnR_4 + SnX \longrightarrow 4R_3SnX$$

$$SnR_4 + SnX_4 \longrightarrow 2R_2SnX_2$$
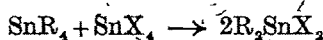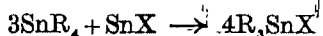
* Part of Thesis approved for the M.Sc. degree of the University of Madras.

Tin tetra-allyl reacts with tin tetrabromide with evolution of heat. Curiously enough tin diallyl dibromide seems to be the main product of the reaction even when theoretical quantities according to the reaction, $3 Sn(C_3H_5)_4 + SnBr_4 \longrightarrow 4(C_3H_5)_3SnBr$ are employed. The reaction,

$$(C_3H_5)_2SnBr_2 + (C_3H_5)_4Sn \longrightarrow 2(C_3H_5)_3SnBr$$
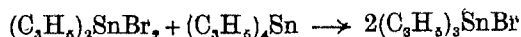
also does not yield pure tin triallyl bromide. Tin diallyl dibromide appears to be found with considerable ease but not the monobromide.

Attempts to prepare tin triallyl hydroxide (*cf.* Grüttner and Krause, *Ber.*, 1917, 50, 1802) and fluoride (*cf.* Krause, *Ber.*, 1918, 51, 1447) from the impure tin triallyl bromide, and tin triallyl iodide by iodination (Goddard and Goddard, *loc. cit.*) of tin tetra-allyl have been unsuccessful.

EXPERIMENTAL

Materials.—In some of the experiments described, B. D. H. allyl bromide was redistilled and used, but on account of the difficulty of obtaining this compound locally, allyl alcohol was prepared from glycerol and oxalic acid and it was converted into allyl bromide

Fig. 1
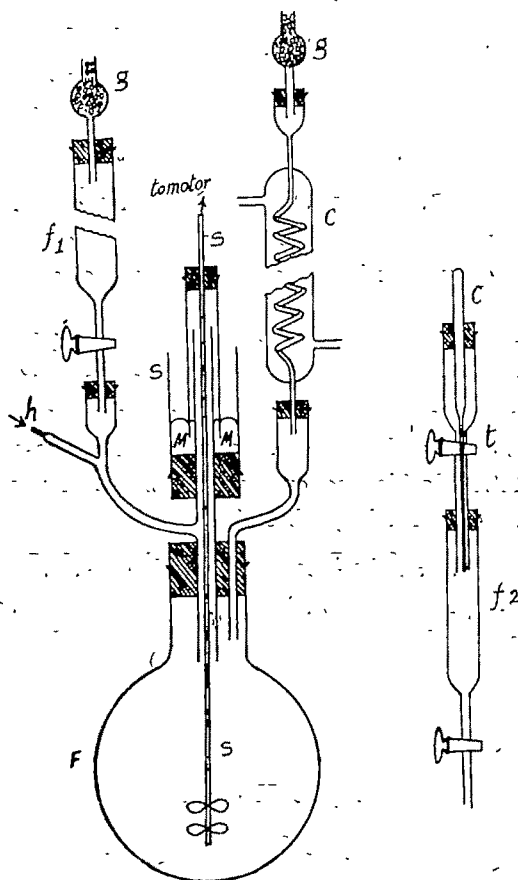
(*Organic Synthesis*, I, 3 ; Vanino, *Praparative Chemie*, II, 27). Commercial ether made an-hydrous by the usual procedure was collected by distilling directly into a long cylindrical funnel f_1 (Fig. 1) from which it was directly added to the flask F_1 (F in figure stands for F_1, F_2 and F_3) in which the Grignard reagent was prepared. Stannic chloride was pre-pared according to the usual method (*Praparative Chemie*, I, p. 594), rectified and distilled in all-glass vessels under reduced pressure and sucked up into weighed glass capsules with capillary necks and sealed. Stannic bromide was prepared by the action of bromine on tin (*Präparative Chemie*, I, 596) and distilled, the fraction distilling at 201° being collected and kept in sealed glass tubes. B.D.H. Analar petroleum ether, b.p 60-80°, kept over sodium wire and distilled before use, was employed as the solvent for the stannic chloride

Isolation of Tin Tetra-allyl.—Dry ether was distilled into the funnel f_1 and about 50 c.c. of it were added to the flask F_1 containing 14.8 g. of magnesium turnings. 26 C.c. (37.2 g.) of allyl bromide were measured into the remaining ether (about 100 c.c.) in f_1. The stirrer, S, was started and the ethereal solution of allyl bromide was added dropwise to the mag-nesium keeping the flask F_1 in iced water to prevent the ether refluxing rather violently. Throughout the experiment pure, dry hydrogen was passed into the apparatus. The addi-tion of allyl bromide took about an hour and a half. The ethereal solution was refluxed for 1 hour and then cooled. The flask F_1 was carefully removed from the apparatus and another flask F_2 of the same size slipped in to prevent the Grignard reagent solution sticking to the sides of the stirrer undergoing decomposition. F_1 was immediately closed with a two holed cork one hole fitted with a tube connected to a source of pure dry hydrogen and another with a tube bent twice at right angles, the second arm carrying a cork fitting a third flask F_3 of exactly the same sized neck as F_1. To a second hole in the cork fitting F_3 a calcium chloride guard tube was fixed. The ethereal solution of the Grignard reagent in F_1 was forced out by pressure of hydrogen into F_3 in order to separate it from the excess of the magnesium turnings. F_2 was then removed from the apparatus and F_3 slid in position. f_1 was then replaced by the funnel f_2 containing petroleum ether. The end of the capillary c passing through tap t was broken by turning the tap and 10 grams of stannic chloride in it driven into the petroleum ether by warming the upper part of c. The Grignard reagent in F_3 was cooled with iced water and stannic chloride solution added drop by drop with stirring. A white solid separated immediately which disappeared on stirring. After all the stannic clolride solution had been added, the mixture was refluxed for 1 hour, the coil condenser C set for downward distillation, and the ether distilled off. The flask and contents were then warmed to about 70° in order to complete the reaction between the stannic halide and the Grignard reagent and to convert any triallyl halide formed into tin tera-allyl by the excess of the Grignard reagent (*vide* Discussion). F_3 was then cooled in ice and salt and the distillate of ether and petroleum ether poured back into it, and ice-cold water added little by little with vigorous stirring. Cold dilute hydrochloric acid (about 3%) was added until the contents of the flask gave two clear layers and the solid deposited on hydrolysis had dissolved. The ethereal layer was separated and the aqueous layer extracted with ether, and dried over calcium chloride.

As the liquid underwent decomposition above 200° it was purified by distilling at reduced pressure from a small bulb with a wide side tube placed near the neck as condenser b.p. 69—70°/1.5 mm. The hot vapours of the liquid were noticed to attack rubber.

Samples of the redistilled substance were analysed. The tin was converted into stannic chloride by heating with excess of concentrated hydrochloric acid in a sealed tube in boiling water and precipitated as stannic sulphide and roasted to stannic oxide. In some of the estimations the tin was directly precipitated as metastannic acid but this method gave lower values, probably because some tin was retained as ammonium hexachlorostannate (cf. Jelley, J. Chem. Soc., 1933, 580). The carbon and hydrogen were estimated by mixing the substance with cupric oxide and " combusting " as usual. [Found : C, 50.99, 51.21 ; H, 7.22, 7.14 ; Sn, 43.36, 42.45 ; M.W., 286 8, 273.4. Sn $(C_3H_5)_4$ requires C, 50.93 ; H, 7.13 ; Sn, 41.98 per cent. M.W., 282.7].

The yield of tin tetra-allyl was 85% of the theory, calculated on the weight of stannic chloride. When stannic bromide was used the yield was only about 60% of the theoretical. Some high boiling hydrocarbon was also obtained.

Tin tetra-allyl is a colourless, highly refractive mobile liquid with a slightly unpleasant odour similar to that of tin tetraethyl. Continued smelling caused sneezing It is soluble in all the common organic solvents and in concentrated aqueous alcohol. It is immiscible with water, and the aqueous suspension on keeping becomes turbid . On cooling in solid carbon dioxide and ether, it does not crystallise but becomes very viscous.

On exposing a drop of tin tetra-allyl in a watch glass for a day it leaves a residue of stannic oxide, but the substance can be kept in sealed tubes for many weeks without any visible change. It burns with a luminous flame forming fumes of stannic oxide. It decolourises solutions of bromine and iodine instantaneously. It is decomposed by concentrated mineral acids evolving propylene, which has been identified by bromination, when propylene dibromide, a liquid with a sweetish odour, b.p 142°, is obtained. With concentrated nitric acid, stannic oxide is precipitated. With fuming nitric acid, the substance inflames with violent reaction leaving a residue of stannic oxide.

Density was determined with a small Hare's apparatus the readings being taken with a travelling microscope and the refractive index was determined with a small hollow prism, $d_4^{10.5} = 1.243$; $\eta_D^{32} = 1.533$; $\eta_a^{32} = 1.526$. Molecular refraction (from Lorentz and Lorenz's formula) for D line $= 70.69$. Molecular refraction for H line $= 69.9$. Calculated using Eisenlohr's (Z. physikal. Chem., 1910, 75, 585) values for D line $= 71.56$; for H_a line $= 71.02$.

Halogen Derivatives

Action of Halogens on Tin Tetra-allyl.—Tin tetra-allyl (5 g.) dissolved in carbon tetrachloride (25 c.c.) was brominated with an approximately $N/2$ solution of bromine in carbon tetrachloride. Both the solutions were first cooled to about —15° with ice and salt. When all the materials were quite dry, a clear solution with a slight yellow tinge was obtained. The carbon tetrachloride was distilled off from a water-bath. A few drops of allyl bromide also distilled at about 70°. This product was distilled at 73-75°/1.5 mm. The liquid seemed to be impure tin triallyl bromide, with tin diallyl dibromide present as an impurity (as shown by analysis for bromine and tin) and it often gave some scaly crystals with pyridine, which is also characteristic of the dibromo compound (vide infra).

This impure tin triallyl bromide possesses a very penetrating odour. It is miscible with all the common organic solvents. Water immediately precipitates an insoluble white solid. On exposing it for a few minutes needle-like crystals in aborescent formation (probably [(C₃H₅)₃SnOH)] ₓ.(C₃H₅)₃SnBr formed by the loss of the hydrogen bromide) are obtained. (*cf.* Krause and Sessions, *J. Amer. Chem. Soc.*, 1925, **47**, 2361). Unlike the other tin trialkyl bromides, this substance did not give any definite compound when pure dry ammonia gas was passed into an ethereal solution. Only a gelatinous precipitate of indefinite composition was formed.

The bromination was conducted using carbon disulphide for pyridine as the solvent and in each case the product was impure tin triallyl bromide. Bromination, when carried out at the temperature of carbon dioxide snow and ether, produced similarly impure reaction products.

The action of iodine on tin tetra-allyl was tried using theoretical quantities of the reactants in carbon tetrachloride solution, both the solutions being cooled in ice and salt. As the iodine solution was being added it was found that some amorphous solid was separating. On distilling off the carbon tetrachloride, a large amount of amorphous solid separated. This was filtered off. A faintly yellow liquid with a very strong penetrating odour was obtained. But solid matter began to separate from the liquid again. Probably the liquid was tin triallyl iodide, which was not stable. Also it did not form any crystalline derivative with ammonia or any amino compound like the other trialkyl iodides of tin (Goddard and Goddard, *loc cit.*)

Action of Stannic Bromide on Tin Tetra-allyl : Formation of Tin Diallyl Bromide.—To tin tetra-allyl (3.5 g.) in carbon tetrachloride (15 c c.) stannic bromide (5.4 g.) dissolved in the same volume of carbon tetrachloride was added and the tube containing the mixture was cooled, evacuated to about 2. c.m. pressure, sealed and kept at 50 ' in a liquid bath for about 10 hours. At the end of the period a test portion showed the presence of free stannic bromide. A few more drops of tin tetra-allyl were added and the heating continued for about 8 hours at the end of which period no free stannic bromide could be detected. On distilling off the carbon tetrachloride under reduced pressure a liquid, b.p. 77-79°/2 mm. was obtained. [Found : Sn, 32.56 ; Br, 43.95. (C₃H₅)₂SnBr₂ requires Sn, 32.93 ; Br, 44.32 per cent].

Tin diallyl dibromide is a light yellow coloured, highly refracting, dense oil with a faintly unpleasant odour. It is soluble in all the common organic solvents. It is decomposed by water and mineral acids. It gives crystalline derivatives with amines.

Pyridine Derivative of Tin Diallyl Dibromide.—To tin diallyl dibromide cooled in water, pyridine was added little by little until there was a faint smell of pyridine. More or less the whole mass solidified. The flat tabular crystals were filtered, washed with a little pyridine, pressed between filter papers and dried over calcium chloride in *vacuo*. The substance melts at 99° (decomp.) with previous softening. The compound is highly soluble in pyridine and decomposes on keeping for some time giving a rather penetrating odour and leaving behind a residue insoluble in pyridine. [Found : Sn, 22.99 ; Br, 30.79 ; N, 5.32, (C₃H₅)₂SnBr₂. 2C₅H₅N requires Sn, 22.89 ; Br, 30.81 ; N, 5.41 per cent].

Tin diallyl dibromide gave a crystalline derivative with aniline also. It is very unstable. The compound, rendered free from aniline, gave differing values on analyses, and it contained an insoluble matter also indicating decomposition.

The author is indebted to Professor Edward Barnes for suggesting and guiding the investigation, and after his demise to Mr. Viswanathan for his continued interest in the work, and for his helpful suggestions. He desires to acknowledge the assitance given by the University of Madras in the form of a Research Scholarship during the tenure of which the latter part of this work was completed.

ORGANOMETALLIC COMPOUNDS OF THE ALLYL RADICAL. PART III
ALLYL DERIVATIVES OF ARSENIC

By K. V. Vijayaraghavan

Triallyl arsine has been isolated by the action of allyl magnesium bromide on arsenic trihalides. Allyl cacodyl also seems to be a product of the reaction. Triallyl arsine and allyl bromide react in acetonitrile solution to form tetra-allyl arsonium bromide. Tetra-allyl arsonium bromide mercuribromide, and tetra-allyl arsonium picrate have been prepared. The quaternary base is also described.

A few organic compounds of aresnic containing the allyl radical are known. On heating mercuric arsenide with allyl iodide in a sealed tube, Partheil and Amort (*Ber.*, 1898, **31**, 596 ; *Arch. Pharm.*, 1899, **287**, 127) obtained tetra-allyl arsonium iodide mercuri-iodide. Mannheim (*Annalen*, 1908, **341**, 223) repeated these experiments and found that the products were double salts of tetra-allyl arsonium iodide and mercuric iodide. A few mixed arsonium compounds containing this radical (Burrows and Turner, *J. Chem. Soc.*, 1921, **119**, 484 ; Dehn and Wilcox, *J. Amer. Chem. Soc.*, 1922, **44**, 810 ; Winmill, *J. Chem. Soc.*, 1912, **101**, 722), and phenyl methyl allyl arsine (Winmill, *loc. cit.*) and dimethyl allyl arsine (Dehn and Wilcox, *loc. cit.*) are also known. Allyl arsonic acid, $C_3H_5.ASO : (OH)_2$ and its sodium salt have also been prepared (Hofmann, *Chem. Zentr.*, 1921, **4**, 1065 ; Quick and Adams, *J Amer. Chem. Soc.*, 1922, **44**, 810).

Triallyl arsine has now been prepared by the action of allyl magnesium bromide on arsenic trichloride in absolute ether medium.

$$6C_3H_5MgBr + 2AsCl_3 \longrightarrow 2As(C_3H_5)_3 + 3MgBr_2 + 3MgCl_2$$
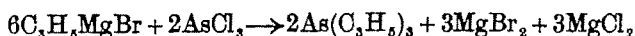
The action of arsenic chloride on allyl magnesium bromide does not seem to be fully represented by the above simple equation. The yield of triallyl arsine is only about 40% of the theoretical. There is an appreciable amount of residue after distilling off the triallyl arsine. This residue fumes in air and in thin layers it burns readily forming fumes of arsenious oxide. It also explodes with oxygen and it has an intensely penetrating odour and is probably allyl cacodyl formed as a by-product.

$$6C_3H_5MgBr + 2AsCl_3 \longrightarrow (C_3H_5)_2As - As(C_3H_5)_2 + C_3H_5.C_3H_5 + 3MgBr_2 + 3 MgCl_3$$
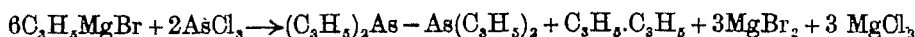
From the residue obtained after distilling off the triallyl arsine, tetra-allyl arsonium bromide and picrate have been prepared, which more or less points to the fact that the residue is allyl cacodyl.

$$(C_3H_5)_2As - As (C_3H_5)_2 + C_3H_5Br \longrightarrow [(C_3H_5)_2AsBr] + (C_3H_5)_3As$$
$$(C_3H_5)_3As + C_3H_5Br \longrightarrow (C_3H_5)_4AsBr$$

$$(C_3H_5)_4AsBr + C_6H_2(NO_2)_3ONa \longrightarrow (C_3H_5)_4AsO.(NO_2)_3C_6H_2 + NaBr$$
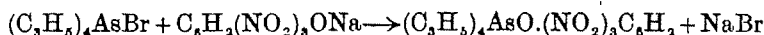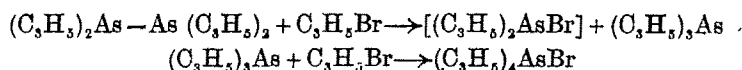
The action of arsenic tribromide on allyl magnesium bromide gives a lower yield than with arsenic chloride.

Richardson and Soper (*J. Chem. Soc.*, 1929, 875) have found that additive reactions of trialkyl amines and alkyl iodides take place very smoothly giving good yields of the tetra-alkyl derivatives in a polar solvent of high cohesion like acetonitrile. Tetra-allyl arsonium bromide has been prepared from triallyl arsine and allyl bromide using acetonitrile as the solvent. Its mercuribromide derivative and tetra-allyl arsonium picrate have also been prepared. By the action of moist silver oxide on the bromide, a strongly alkaline syrupy

liquid is obtained which is confirmed to be the hydroxide by the preparation of tetra-allyl arsonium picrate from it.

$$(C_3H_5)_4AsOH + C_6H_2(NO_2)_3OH \longrightarrow (C_3H_5)_4AsO(NO_2)_3C_6H_2 + H_2O.$$
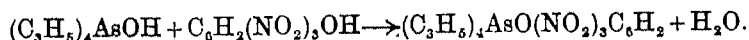
· Thus a study of the symmetrical allyls of the three metals, mercury (*J. Indian Chem. Soc.*, 1940, **17**, 589), tin (*ibid.*, 1945, **22**, 135) and arsenic show that these compounds possess properties similar to other metal-alkyls and that the radical $CH_2 : CH.CH_2$ be-· haves in organometallic combination more or less similarly to the other alkyl radicals.

The metal-allyls undergo all the reactions characteristic of other metal-alkyls. It is interesting to note that both mercury diallyl and tin tetra-allyl part with one allyl radical with halogens, like bromine, in exchange for a halogen atom.

$$Hg(C_3H_5)_2 + Br_2 \longrightarrow C_3H_5HgBr + C_3H_5Br$$

$$Sn(C_3H_5)_4 + Br_2 \longrightarrow (C_3H_5)_3SnBr + C_3H_5Br$$
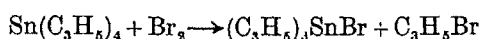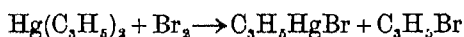
but do not form derivatives with one or more allyl radicals saturated by bromine, as for example, $CH_2Br.CHBr.CH_2HgC_3H_5$ or $(CH_2Br.CHBrCH_2)_2Hg.$

Halogen hydracids also affect these metal allyls in exactly the same way as they react with other metal alkyls. The action with the reactive hydrogen gives an indication of the comparative reactivity of organometallic compounds. Mercury diallyl is easily decomposed by dilute hydrochloric acid (about 4%). Tin tetra-allyl is not acted upon by dilute hydrochloric acid except on heating, while concentrated acid decomposes it easily in the cold, whereas moderately concentrated hydrochloric acid decomposes arsenic triallyl only on boiling. The order of reactivity is in agreement with what one would expect. Relative reactivities depend upon the strength of the carbon-metal bond in the organometallic molecule and this latter can be correlated with the metallic nature of the central atom. With enhanced metallicity the bond would become weaker (*cf.* Gilman and Yale, *Chem. Rev.*, 1942, **30**, 181).

It is surprising to note that mercury diallyl is not stable as was expected. The ethereal solution of the substance is fairly stable Possibly the substance exists as a co-ordination complex in solution, as the Grignard reagents do, thus completing an octet round the central atom.

$$
\begin{array}{ccc}
C_3H_5 \diagdown & & \diagup O(C_2H_5)_2 \\
 & Hg & \\
C_3H_5 \diagup & & \diagdown O(C_2H_5)_2
\end{array}
$$
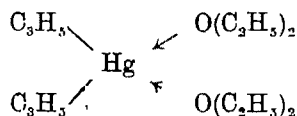
.Tin tetra-allyl seems to be comparatively stable. This is to be expected as the central atom has a complete octet round it and quite probably it will behave as a perfectly non-polar liquid on account of the symmetrical structure of the compound.

Ammonia and phosphine do not combine with oxygen or chlorine directly to form compounds like $NH_3 \longrightarrow O$ or $NH_3 \longrightarrow Cl_2$ but substituted amines and phosphines form such compounds. The tendency of the unshared electron pairs in these compounds to be engaged in donor activity is enhanced by substitution. In satuated systems this activity is of course restricted to the hetero atom, but in an unsaturated system it may be transmitted through an intervening chain on account of the polarisability of the double bonds. Arsenic triallyl

shows a great tendency to unite with oxygen of the air. It combines with oxygen of the air quite readily, most probably forming the triallyl arsine oxide $(C_3H_5)_3$ As$\longrightarrow$O. The compound could not be prepared by exposing triallyl arsine to air as the product was contaminated with other oxidation products and gave a sticky mass. Other trialkyl arsines also behave similarly when exposed to air (Cahours, *Annalen*, 1864, **112**, 230; Landolt, *Annalen*, 1854, **89**, 329). Triallyl arsine also readily combines with allyl bromide to give the tetra-covalent ion [$(C_3H_5)_4$As]$^+$. The bromide is completely ionised in solution.

The alkalinity of the alkyl substituted bases like $(CH_3)_4$NOH or $(CH_3)_4$POH is greater than that of ammonia or phosphine. Tetra-ethyl arsonium hydroxide is quite a strong base precipitating hydroxides of heavy metals and liberating ammonia from ammonium salts (Landolt, *loc. cit.*). Tetra-allyl arsonium hydroxide is found to be alkaline to litmus and it precipitates hydroxides of copper and silver from the respective salts, but it does not liberate ammonia from ammonium salts. The basic nature of this quaternary base is less than that of the other tetra-alkyl arsonium hydroxides. This might be explained on the basis of the possibility of resonance between an arsenic atom and an unsatuarated radical, just as the introduction of a phenyl group weakens the basic nature of ammonia.

EXPERIMENTAL

The arsenic chloride was prepared by the usual method of passing dry chlorine over heated arsenic and the arsenic bromide by the action of bromine on arsenic; these were purified by two distillations, and sucked up into weighed tubes with capillary necks and sealed. The allyl magnesium bromide was prepared as described by the author (previous part).

To the Grignard reagent from allyl bromide (28 g.) in absolute ether (250 c.c.) cooled to —15° with ice and salt, arsenic chloride (7 g.) dissolved in dry ether (50 c.c.) in the funnel f_2 (*vide* Part II) was added drop by drop with vigorous stirring. After all the arsenic chloride solution had been added, the mixture was allowed to warm up gradually to room temperature. A solid gradually appeared. It was found when concentrated solutions were used, too much solid separated all of a sudden and the stirrer got stuck up. The flask F and contents were left at room temperature for about 15 minutes. They were then cooled in ice and salt, and ice-cold ammonium chloride solution was added little by little with stirring. Cold dilute hydrochloric acid (about 3%) was added until the contents of the flask separated into two layers and the solid deposited on hydrolysis had dissolved. The ethereal layer was separated and the aqueous layer extracted with ether and the extracts dried over anhydrous sodium sulphate in an atmosphere of carbon dioxide or sometimes hydrogen overnight.

The ethereal layer was siphoned into a two-necked flask under pressure of carbon dioxide. To one of the necks was fitted an one-holed cork carrying a delivery tube leading to a condenser and to the other a two-holed cork through one of which passed an inlet tube for carbon dioxide, and through the other, a weighed capsule with a drawn out neck. The ether was distilled off in a carbon dioxide atmosphere and the pale yellow coloured residual liquid was sucked up into the capsule, sealed, and preserved for use.

Since the liquid showed signs of decomposition in ordinary vacuum distillation, and was found to absorb oxygen from the atmosphere, it was distilled *in vacuo* twice in one

FIG. 1
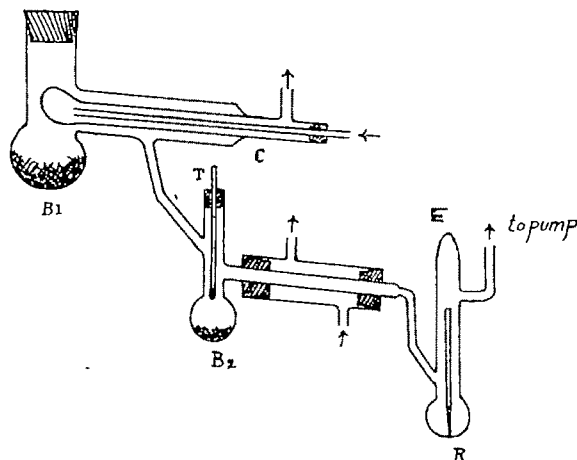
operation in a special all-glass apparatus (see Fig. 1) which is an adaptation of a molecular still (Morton, "Laboratory Technique in Organic Chemistry", International Chemical Series, p. 120). The liquid in B_1 with enough glass wool to prevent bumping was distilled from the water-bath at 50° at a pressure of 2 mm., the air in the apparatus being originally displaced by dry nitrogen. The condensate collecting at the internal joint C, was tilted down into B_2 and re-distilled. The liquid distilled at 41° and collected in R in which weighed capsules (only one shown in the figure) containing deep file marks were kept inverted before drawing off and sealing the open end E. On admitting dry nitrogen into the evacuated apparatus, the capsules got filled up with the liquid. The receiver R was cut open along a file mark below E and the capsules were taken out, carefully sealed immediately and used for analysis.

A capsule containing a weighed amount of the liquid was broken in concentrated hydrochloric acid in a long tube, and the tube was sealed and heated at 100° for about $\frac{1}{2}$ hour and at 150° for another $\frac{1}{4}$ hour. The arsenic chloride solution so obtained was diluted, and the arsenic precipitated as arsenic sulphide and the precipitate dried at 105° to constant weight. For the combustion of the substance the last few centimeters of the usual cupric oxide filling of the combustion tube was replaced by lead peroxide which at the temperature of the furnace formed red lead, and retained the arsenic as lead arsenate (Falkov and Raiziss, *J. Amer. Chem. Soc.*, 1923, 45, 998). The capsule containing the substance which had a deep file mark, was placed in a combustion boat and just before the boat was pushed in, a crack was started on the file mark by a red hot glass point. (Found: C, 54.67, 54.33; H, 7.59, 7.73; As, 37.72, 38.02. $As(C_3H_5)_3$ requires C, 54.51; H, 7.63; As, 37.84 per cent).

Triallyl arsine is a colourless, mobile liquid with a slightly penetrating odour. It is soluble in all the common organic solvents. It absorbs oxygen from the air with slight evolution of heat forming probably the oxide. On exposing the substance to air it becomes cloudy and gradually turns into a brown sitcky mass. But the substance can be preserved in sealed ampoules in an atmosphere of an inert gas like nitrogen or carbon dioxide. It decolourises bromine and iodine in organic solvents. With strong mineral acids, the arsenic

is converted into the inorganic form with evolution of propylene, which was identified as the dibromide, b.p. 142°.

Tetra-allyl Arsonium Bromide.—To triallyl arsine (2 g.) dissolved in dry acetonitrile (10-15 c.c.) was added allyl bromide (2.4 g.) in acetonitrile (10-15 c.c.). The tube containing the mixture was cooled in ice water and evacuated to about 2 c.m. pressure, sealed and heated for about 6 hours at 60°. The acetonitrile solution was diluted with dry ether (200-300 c.c.) when the solution became turbid. The suspension was kept in cold storage (5° C) overnight. An oily liquid separated at the bottom. The ether was siphoned off and the last traces of ether removed by evaporation *in vacuo*. The oily liquid crystallised in felted needles or platelets on cooling in ice and salt and scratching the liquid. The crystals could not be separated as on pressing them they melted. They were also highly hygroscopic. On allowing the crystals to warm up and melt between 40-50° to remove absorbed solvent (at reduced pressure) they underwent partial decomposition as shown by the formation of solid matter insoluble in acetonitrile. The substance appeared to be tetra-allyl arsonium bromide with acetonitrile of crystallisation. It was highly soluble in water, alcohol, acetonitrile etc., and contains ionic bromine.

Tetra-allyl arsonium bromide mercuribromide was prepared by adding an alcoholic solution of mercuric bromide to an alcholoic solution of tetra-allyl arsonium bromide. A white coarsely crystalline substance separated immediately. The solution was cooled, the crystals filtered and washed with alchlolol, m.p. 66°. It crystallised from acetone in small plates. It is highly soluble in acetone and sparingly in alcohol.

The bromine was estimated by Piria and Schiff's method. For the mercury estimation the substance was warmed with 1-2 c.c. concentrated nitric acid ; the solution diluted and filtered and hydrogen sulphide passed to saturation. To the orange coloured mixture of precipitates about 10 c.c. of yellow ammonium sulphide were added and the mercuric sulphide washed with sodium sulphite to remove traces of sulphur and dried at 105-110° to constant weight. [Found : Br, 35.99 ; Hg, 29.17. $(C_3H_5)_4AsBr.HgBr_2$ requires Br, 36.29 ; Hg, 29.52 per cent].

Tetra-allyl arsonium picrate was prepared by adding a saturated aqueous solution of sodium picrate to an alcoholic solution of tetra-allyl arsonium bromide. A yellow precipitate was obtained which gradually became crystalline on adding a few drops of alcohol and cooling. The crystals were washed with ice-cold water, and dried over calcium chloride *in vacuo*, m.p. 82.5°. It is soluble in alcohol but sparingly soluble in ice-cold water. A weighed amount of the substance was heated with 5 c.c. of fuming nitric acid in a Carius tube and the arsenic acid so obtained precipitated as $MgNH_4AsO_4, 6H_2O$ (Dick, *Z, anal. Chem.*, 1934, **98**, 429) by adding magnesia mixture, and excess of ammonia to strong alkaline reaction and allowing to stand in a refrigerator overnight. [Found : As, 15.82. $(C_3H_5)_4AsO(NO_2)_3C_6H_2$ requires As, 16.05 per cent].

Tetra-allyl Arsonium Hydroxide.—To a concentrated aqueous solution of tetra-allyl arsonium bromide moist silver oxide was added little by little. The brown colour of the oxide changed to yellow gradually. A small excess of silver oxide was added and the mixture agitated, allowed to stand for some time and filtered. The solution was alkaline and probably contained tetra-allyl arsonium hydroxide. On evaporating over sulphuric acid in a vacuum desiccator, a syrupy liquid was obtained.

The aqueous solution precipitated copper and silver hydroxides from their respective salts, but did not liberate ammonia from ammonium salts. To the above concentrated solution of the base a saturated aqueous solution of picric acid was added. A crystalline yellow solid separated, m.p. 82.5° (mixed m.p. with tetra-allyl arsonium picrate).

Allyl Cacodyl.—The appreciably large amount of residue in B_1 obtained after distilling off the triallyl arsine was examined. The glass wool which was put in the distilling liquid to prevent bumping fumed in air and burned forming fumes of arsenious oxide. On being dropped into a jar of oxygen it exploded violently producing black particles of carbon and arsenious oxide. That the residual liquid was probably allyl cacodyl was shown as follows.

The glass wool wet with the residue, after distilling off the triallyl arsine completely, was quickly washed with ether and to the ethereal extract a few g. of allyl bromide added and the solution heated to about 60-70°. A syrupy liquid was obtained. A portion of it was dissolved in alcohol and a concentrated aqueous solution of sodium picrate was added. The crystalline substance obtained melted at 82.5° (m.p. of tetra-allyl arsonium picrate).

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STUDIES IN GLASS SYSTEMS. MAGNETIC SUSCEPTIBILITY OF POLAR CRYSTALS DISSOLVED IN BORAX GLASS

By Subodh Kumar Majumdar and Hemlal Saha

The magnetic susceptibility of solid systems consisting of LiCl, NaCl and KCl dissolved in borax glass at different concentrations has been measured and the value for the dissolved alkali halide has been calculated from the additivity formula. These values show departure from their normal values as would be expected from the Fajans theory of deformation applied to solid solutions. But the variation is in an opposite sense as would be expected from theoretical considerations.

Majumdar and co-workers (Wulff and Majumdar, *Z. physikal. Chem.*, 1936, **31**, 319 ; Majumdar and Sarma, *J. Indian Chem. Soc.*, 1942, **19**, 461) have studied polar crystals like alkali halides dissolved in B_2O_3 glass. Using the mole-refraction method,, they have found that the Fajans rule of deformation holds good *qualitatively* in solid solutions of alkali halides dissolved in glass systems. In the present paper, the magnetic susceptibility of the three salts, LiCl, NaCl and KCl, dissolved in fused borax glass at different concentrations, have been determined by Guoy's method.

The relation between the magnetic properties of a substance and its internal structure has of late received very considerable attention. The salts studied in this paper are all diamagnetic having ions with inert gas configurations. It is interesting to note whether the magnetic susceptibility of these salts vary with concentration in the glass and, if so, at what rate.

It is well known that Pascal in his classical work, working mostly with nonpolar substances laid down the additivity formula for the diamagnetic susceptibility of molecules. If χ_M be the molecular susceptibility of a diamagnetic molecule, then according to Pascal,

$$\chi_M = A\Sigma\chi_A + \lambda, \text{ where } A\Sigma\chi_A$$

is the sum of the atomic susceptibilities and λ is the constitutive constant depending on the nature of the linkage. Whether Pascals' law holds good for all compounds, including polar compounds in the solid state and in state of solution, has formed the subject matter of numerous investigations in recent years.

Although very extended investigations have been made concerning magnetic properties of alloy systems, solutions of salts and to a limited extent the solid salts themselves, little work seems to have been done with binary systems of salts. The former has been studied among others by Honda and Sone (*Sci. Rep., Tokuhu Imp. Univ.*, 1913, **2**, 1 ; 1925, **14**, 479), Garrison (*J. Amer. Chem. Soc.*, 1925, **47**, 622), Spencer and John (*Proc. Roy. Soc.*, 1927, **116**, A, 61) and with binary systems of salts by Bhatnagar and Kapur (*J. Indian Chem. Soc.*, 1932, **9**, 347). They examined the magnetic properties of solid solutions of $KMnO_4$—$KClO_4$, KCl—NaCl, KBr—KCl and KBr—NaBr systems and found that in the system $KMnO_4$—$KClO_4$ the susceptibility-concentration curve is a straight line, while in the remaining systems curved graphs are obtained. In other words the susceptibility-concentration curves may either follow a linear course or the curve may pass through a

maximum. These workers have tried to correlate the heat of formation of the systems with their magnetic susceptibility. When the heat of formation is zero, the susceptibility-concentration curve is a straight line; in other cases the curve passes through a maximum. This point is of some importance in the present investigation. As will be seen later, the susceptibility-concentration curves become linear when the salts in different proportions are simply intimately mixed with borax, while a different type of curve is obtained when the same system is previously melted.

<center>EXPERIMENTAL</center>

The salts from which the samples were prepared were Merck's *pro Analyse* variety excepting LiCl which was specially purified. The latter, which was extremely hygroscopic, was heated in a platinum basin and the dried mass digested with a mixture of absolute alcohol and ether, in which only LiCl dissolved. The solution was filtered and the filtrate evaporated to dryness. Before preparing a sample for measurement, the salt was kept at a high temperature for several hours. The other salts were carefully dehydrated for a pretty long time.

Borax was powdered and kept in thin layers in an air oven for several hours until a little portion of it digested with absolute alcohol did not give coloration with anhydrous copper sulphate. The anhydrous borax was then kept in a vacuum desiccator for several days.

Different samples were prepared by taking the dehydrated borax and alkali halide in varying proportions in a platinum crucible and heating to temperature of 900-1000° for eight to ten hours until a thoroughly homogeneous melt was obtained. A portion of the ingredients sublimed off before melting but afterwards a melt of constant composition was obtained. The crucible was then chilled by placing it on a cooled surface when the solidified mass cracked. The solid was then detached, transferred to a sample tube and preserved in a vacuum desiccator until use. The samples presented a thoroughly transparent appearance even after several weeks. Each sample was examined under crossed Nicols in a polarising microscope; it remained dark in all positions indicating that although borax crystals were anisotropic, its glass was isotropic. Before each experiment, the pieces were powdered in an agate mortar.

Analysis of the Samples.—The chlorine content of the samples was determined volumetrically in nitric acid solution by back titration method. A definite weight of the glass was dissolved in hot water and excess of nitric acid added. A check was made in the case of the NaCl—$Na_3B_4O_7$ systems by estimating the total amount of sodium as Na_2SO_4 by repeatedly heating with HF and H_2SO_4. The total sodium content fairly agreed with the sodium in borax and sodium chloride.

Determination of the Magnetic Susceptibility of the Samples.—The magnetic susceptibility of the samples was determined by Guoy's method in the Chemistry Department of the University College of Science, Calcutta. A constant current of 5 amp. checked by an ammeter and rheostat was passed. Blank experiments were done with the empty tube. The mass susceptibility χ_m was calculated from the following formula (Klemm " Magnetochemie ")

$$\chi_m = 2.lx/mH_{max}^2.1.019$$

where χ_m is the susceptibility per unit mass of the substance (expressed in C.G.S. units per g.)

l is the length of the column of the substance in cm.

x is the change in weight in mg. and m is the weight of the substance in g.

H_{max} is the maximum strength of the magnetic field in Gauss. (In this case $H_{max} = 10.4 \times 10^3$ Gauss—determined against conductivity water as the reference substance. $\chi_g = -0.72 \times 10^{-6}$).

Care was taken to pack the substance as uniformly as possible by tapping, but this always left a source of error. The calculated values of the susceptibility of the alkali halides were determined from the additivity formula

$$100\chi_g = p + \chi_1 + (100 - p)\chi_2;$$

where χ_g^{11} is the observed mass susceptibility of the glass system,

χ_1 is the mass susceptibility of the dissolved alkali halide (to be calculated).

p is the percentage of the alkali in the glass, and

χ_2 is the mass susceptibility of the fused borax, it being assumed that the susceptibility of the borax in the glass remains unaltered. This last assumption has to be made (as is usually done) in all two-component systems, as for example in aqueous solutions. Otherwise the variation of both cannot be studied from a single equation. This method is used in calculating mole-refraction and specific refraction as well.

A second series of measurements was made by weighing out different quantities of fused borax and NaCl and fused borax and KCl, powdering each sample in an agate mortar without fusing and determining the magnetic susceptibility as before. Lithium chloride could not be tested in this manner because of its extreme hygroscopic nature. The susceptibilities of the pure substances were determined by Guoy's method in the same way and compared with the values given in the International Critical Tables and those determined by Bhatnagar and Mathur by the Int. balance.

TABLE I

MASS SUSCEPTIBILITY × 10⁶

Salt.	Guoy method.	International Critical Table.	Bhatnagar and Mathur.
LiCl	—	—0.572	—
NaCl	—0.4898	—0.499	—0.4902
KCl	—0.5206	—0.516	—0.5031
Borax glass	—0.4073	—	—

The susceptibility of salts determined by different workers vary presumably because of traces of paramagnetic impurities, uncertainty about dehydration and also because of the errors inherent in the different methods. The values in the first column are taken for our calculation; although not quite accurate, these will not seriously vitiate *comparative results*.

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In the following tables, the observed mass susceptibilities of different samples of glasses are recorded in column 2 ; in column 3, the mass susceptibility of the dissolved halide calculated from additivity formula are given.

TABLE II

LiCl—BORAX GLASS

LiCL	Mass susceptibility $\times 10^6$		
	Obs for glass.	Calc. value for dissolved LiCl.	Value for LiCl (pure).
7.103%	—0.4248	—0.653	—0.572
8.365	—0.4295	—0.685	(Inter. Crit. Table)
11.490	—0.4408	—0.698	
13.05	—0.4562	—0.782	

TABLE III

NaCl—BORAX GLASS

NaCl.	Mass susceptibility $\times 10^6$		
	Obs. for glass.	Calc. value for dissolved NaCl.	Exp. value for NaCl (pure).
11.72%	—0.4280	—0.592	
12.25	—0.4513	—0.766	
16.27	—0.4613	—0.739	—0.4898
17.02	—0.4624	—0.731	
18.97	—0.4703	—0.730	
19.95	—0.4714	—0.728	

TABLE IV

KCl—BORAX GLASS

KCl.	Mass susceptibility $\times 10^6$		
	Obs. for glass.	Calc. value for dissolved KCl.	Exp. value for KCl (pure).
11.92%	—0.4373	—0.659	
13.31	—0.4439	—0.682	—0.5206
15.20	—0.4460	—0.662	
18.63	—0.4470	—0.620	

In the following tables, the mass susceptibility values of mechanical mixtures of NaCl-borax and KCl-borax are recorded. In column 2, the experimental value is given and in the last column, the value calculated from the additivity formula are recorded.

TABLE V

NaCl—BORAX GLASS MIXTURE

NaCl	Mass susceptibility $\times 10^6$	
	Obs.	Calc.
11.01%	—0.4250	—0.4163
12.50	—0.4278	—0.4175
14.00	—0.4296	—0.4183
16.00	—0.4306	—0.4206
18.02	—0.4379	—0.4222

TABLE VI

KCl—BORAX GLASS MIXTURE

KCl	Mass susceptibility $\times 10^6$	
	Obs.	Calc.
12.95%	—0.4182	—0.4219
13.31	—0.4101	—0.4223
14.53	—0.4246	—0.4235
16.00	—0.4275	—0.4255
18.11	—0.4348	—0.4279

DISCUSSION

Majumdar and co-workers have studied the change in mole-refraction and lattice distances of various alkali halides dissolved in boric oxide and borax glasses. The general conclusion arrived at by them are as follows : (*i*) Salts are more strongly deformed in glass systems than in corresponding aqueous solutions, and (*ii*) the deformation of the anion by the cation follows Fajans' deformation rule fairly accurately. Hence the deforming power of the cation on a common anion may be expressed by· the inequality $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$.

Whether strict additivity relation exists in the case of solid diamagnetics has been studied among others by Gray (*Phil. Mag.*,· 1930, *iv*, **10**, 191 ; Dakers, *ibid.*, 1931, *iv*,, **11**, 81), Farquharson (*ibid.*, 1932, *iv*, **12**, 283) and Kido (*Sci. Rep.*, *Tokuhu Univ.*, 1932, **21**, 149, 288, 869). Kido believes that the additivity relation exists in the case solid ionic crystals and drew up a table of ionic susceptibilities on this assumption. Hocart (*Compt. rend.*, 1929, **188**, 1151) has made a careful measurement, taking particular care about the purity of the salt. The following table shows the values of molecular susceptibility of some salts studied by them.

TABLE VII

MOLECULAR SUSCEPTIBILITY

Salt	Kido	Hocart	Gray & Farquharson
NaCl	29.6	30.1	..
KCl	35.8	39.1	39.1

The values obtained by us are 28.63 for NaCl and 38.82 for KCl. (for NaCl, $\chi_M \times 10^6 = 0.4898 \times 58.46 = 28.63$; for KCl, $\chi_M \times 10^6 = 0.5206 \times 74.56 = 38.82$) The strict additivity rule which was assumed by these workers for ionic crystals cannot however hold good *absolutely*, because the outer electron density distribution of the ions in the crystals must be different from those of free ions. If χ_F, χ_C, χ_D represent respectively the values of magnetic susceptibility of the free ion, crystal and in solution respectively, then both χ_C and χ_D would be less than χ_F owing to the mutual interaction effects, which will bring about a change in electron density distribution, on which diamagnetism primarily depends. Brindley (*Phil. Mag.*, 1931, *iv*, **11** 786) has discussed magnetic data from the standpoint of *effective ionic radii*, which are conditioned by the effective spread of electron density caused by surrounding ions or molecules. The diamagnetic susceptibility therefore gives a good indication of the space-charge distribution within the molecule.

Referring to our results, we find a smooth curve for suceptibility-concentration graphs for LiCl and KCl, whereas for NaCl the curve is not so smooth. One would naturally expect a smaller value of susceptibility for dissolved salts in the glass systems than in the pure crystalline state and this divergence should be maximum in the case of LiCl and decrease with the increase of the diameter of the cation (Fajans rule). Here we· find however although the deviation of the value is most marked in the cases of all the three. salts investigated by us, it is *in an opposite sense* to what would be expected from theory, For while the value of mass susceptibility of pure LiCl is —0.572×10^{-6}, the value calculated from the mixture

FIG. 1

Solid soln.
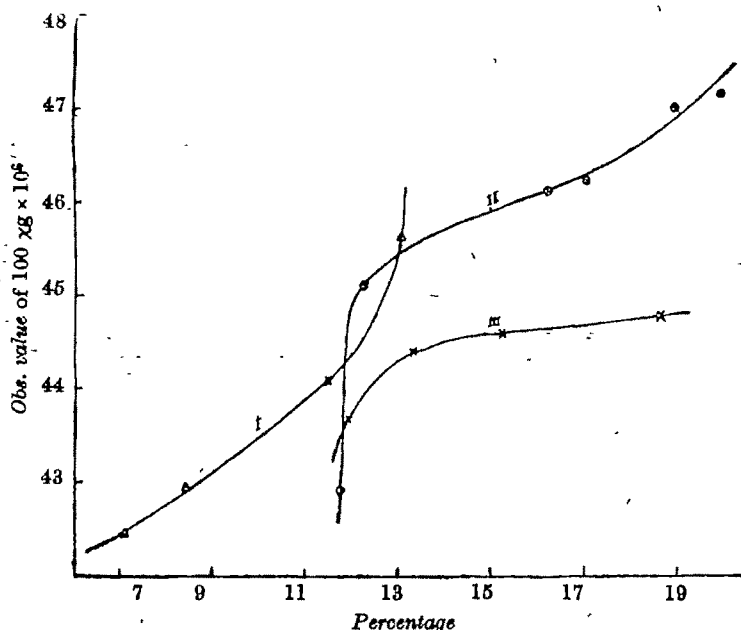
Curves I—III refers respectively to LiCl, NaCl and KCl

law varies between —0.653 and —0.782 ($\times 10^{-6}$) and this is also true, more or less, for the other salts. Another point to note in this connection is that in the case of LiCl, as well as in the case of NaCl and KCl, the value of the pure salt which would be obtained from extrapolation of the curves would have much higher negative values than the experimental values of the pure salts themselves. In the case of NaCl, the calculated value in the glass changes from —0.592 for a concentration of 11.72% to —0.728 $\times 10^{-6}$ corresponding to a concentration of 19.95% of the salt. The susceptibility-concentration curve unlike that of LiCl seems to be definitely bent. In the case of KCl, the calculated value of the susceptibility of the salt dissolved in the glass varies from —0.659 for a concentration of 11.92% to —0.620 $\times 10^{-6}$, corresponding to a concentration of 18.63% of the salt.

Comparing the changes in suceptibility for unit change in concentration in the region of about 11.5—11.9% of the salt we get the following figures for the three salts :

$$\text{LiCl,} —1.09 \times 10^{-2} \text{ ; NaCl,} —8.7 \times 10^{-3} \text{ and KCl,} —1.16 \times 10^{-2}.$$

In conformity with the mole-refraction data, one would expect the greatest change in the case of LiCl and least in the case of KCl. As has been stated before a decrease would be expected in every case, which is not an experimental fact. Moreover, KCl behaves also in anomalous manner. Whether this abnormal behaviour of this salt is due to inherent defects in the measurement or due to the presence of paramagnetic impurities has still to be decided.

Whether the glass systems studied by us represented simple solid solutions as in the case of alloys (simple) or homogeneous mixtures was further studied. LiCl had to be excluded from the investigation on account of its hygroscopic nature. As has been found

by Bhatnagar and Kapur (*loc. cit.*), the susceptibility-concentration curves are straight lines in the case of mixtures of salts which are not isomorphous and do not form solid solutions, whereas in these cases the curve passes through a maximum. The susceptibility-concentration curves of mixtures for NaCl and KCl are almost straight lines, the slight devia-

FIG. 2

Mixture.

Percentage
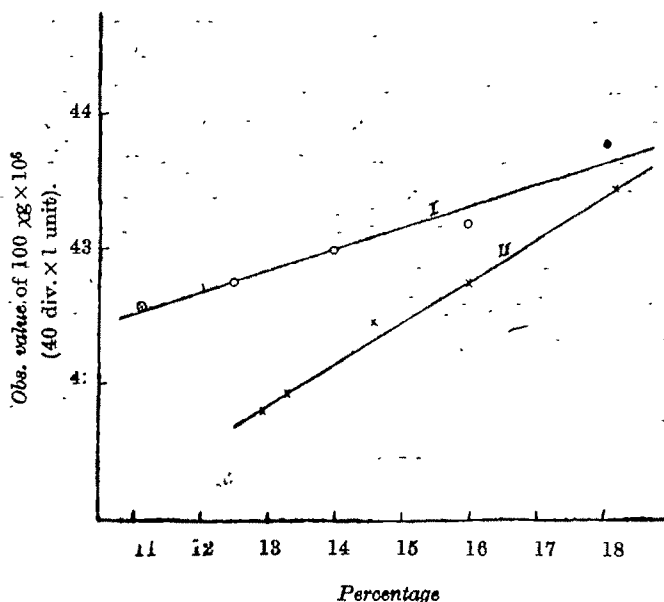
Curves I—II refer respectively to NaCl and KCl.

tions being due to experimental error. We can infer therefore that the systems previously studied are not simple mixtures following the additivity rule. In these cases however the explanation give by Bhatnagar and Kapur is inapplicable, as apart from the difference in formula type (XCl—$Na_2B_4O_7$) the molecular volumes are wide apart from that of the borax glass as would be seen from the following :

Substance		LiCl	NaCl	KCl	$Na_2B_4O_7$
Mol. vol. (c.c.)	..	20.60	27.02	37.57	85.43

The conditions for isomorphous mixture are absent here.

Majumdar and Palit (*loc. cit.*) have shown that when polar crystals like NaCl are dissolved in a glass, the lattice structure of the former still persists ; there is however a widening of the lattice distance. This has been further confirmed in the case of KCl (to be published in a separate communication). It is suggested by the authors that the increase in the lattice distance of the alkali halides is due to some sort of shielding action of the glass molecule on the electrostatic forces operating within the crystal. Roughly this means the Coulomb forces are weakened on account of the higher dielectric constant of the solvent medium. Whether the dielectric constant alone is sufficient to explain the change in lattice distance has still to be decided, but it is clear that this will also bring about a change in other physical properties like magnetic susceptiblity, which is actually found to be the case.

The question in which state the dissolved salt exists in the glass has now to be discussed. Zachariasen, Warren and others believe that a *non-periodic* arrangement of the constituents obtains in the glass as opposed from a strictly periodic lattice arrangement of the same substance in the crystalline state. This is the reason why diffuse bands or haloes are obtained in X'ray diffraction photographs with glass instead of sharp lines as with crystalas. It has been further established by Warren that in the case of borax and boric oxide glasses, the three valencies of the boron atom are arranged in a triangular manner and the linking is through oxygen atoms. In some cases the co-ordination number is found to increase. The cations of borax glasses like Na^+, K^+ are supposed to lie in the empty spaces of this non-periodic network. In this case we might suppose that a regular periodic lattice of the alkali halide is formed within the glass, the alkali and the halogen ions taking up their positions in the empty spaces of the network in a three dimensional sense.

The forces operating between two neighbouring ions in a polar crystal are partly attractive (Coulomb forces) and partly repulsive (Born forces). Both of these forces will be affected by the surrounding atmosphere and the magnetic susceptibility of the crystal dissolved in a glass may be expected to be altered which is found to be the case experimentally. Further work on the subject is in progress.

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THE APPLICATION OF ELECTRONIC THEORY TO EXPLAIN ORGANIC REACTIONS AND TO PREDICT OTHERS. PART I. DYES

By SAIYID SHAMIM AHMAD

The present paper is an attempt at making use of the Electronic Theory as the basis of predicting unknown reactions, and explaining the already known facts and the empirical Nietzke's rule derived therefrom.

An attempt is also made to increase the classes of compounds which couple with diazo compounds. In this respect some preliminary results are given which indicate that the predictions made may not be untrue. A new class of compounds *i.e.* the acyl amides are predicted to be capable of being dizaotised.

It is evident that only electric force can explain the large energy changes involved in chemical reactions. Therefore the fundamental theory of chemistry must be based upon the properties of the electrons. Unfortunately the opinion is generally held that the Electronic Theory, though admirable for purposes of explaining the existing data, cannot be used as a basis for predicting the course of reactions and forecasting unknown reactions. As verification of predictions is the test of a theory, the following work was taken up to remove the above objection. It is hoped to modify the theory if results are obtained contrary to predictions.

Colour and Structure.—OH, NH$_2$ and Cl are supposed to possess lone pairs of electrons. These electrons are supposed to have the property of conjugation with suitable system of bonds as in aromatic compounds. Thus their influence can easily be transported to *ortho* or *para* position. This conjugation of the lone pair of electrons with the aromatic nucleus facilitates attack on *ortho* and *para* positions by electrophilic reagents. This is the mechanism of the *ortho* and *para* substitution in the benzene series.

In the Theory of Colour and Structure it is found that OH and NH$_2$ can behave as auxochromes. It is evident that Cl-, Br- and I- are very similar to the above two groups, in having lone pair of electrons conjugated with the aromatic nucleus. If the hypothesis is made that the colour is due to the resonance caused by the conjugation of the lone pair of electrons it becomes evident that :—

(*i*) Cl-, Br-, I- should also behave as auxochromes.

(*ii*) As the distance of the nucleus increases from the outer orbit, the auxochromic properties should increase.

(*iii*) Similarly the auxochromic properties should be NH$_2$<NHCH$_3$<NHC$_2$H$_5$< N(C$_2$H$_5$)$_2$ as this is the order of the availability of electrons.

Again, in the amide grouping CONH$_2$
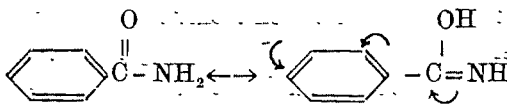
it is found that the compound can assume a form in which the lone pair will have the opportunity of conjugating with the aromatic nucleus.

(*iv*) Thus CONH$_2$ group should behave as an auxochromic group.

(*v*) Similarly CONHOH group should also behave as an auxochrome.

These predictions of behaviour have already been noted. Thus Nietzkes' rule is easily explained on the basis of this theory.

(*i*) Cl- has got auxochromic properties. Thus dinitrobenzene is colourless while chlorodinitrobenzene is pale yellow, Cl- being a weak auxochrome due to its greater nuclear charge.

(*ii*) Iodo compounds are more deeply coloured than Br- compounds which are more deeply coloured than the chloro compounds (Nietzke's rule).

(*iii*) The intensity of the colour increases in the anticipated order : $N(C_2H_5)_2 >$ $NHC_2H_5 > NHCH_3 > NH_2$ (Nietzke's rule).

(*iv*) $CONH_2$ is well known for enhancing the colour of the azo compounds.

Coupling.—Only six classes of organic compounds are known to couple with diazotised aromatic amines. With the exception of hydrocarbons and compounds containing active methylene group all the other classes of compounds are either phenols and amines or are their derivatives. On similar considerations as above it can be predicted that Cl-, Br-, I-, $CONH_2$ and $CONHOH$ groups when present in the aromatic neclous of an aromatic compound should lead to its coupling with diazonium salts.

Preliminary experiments performed with *p*-nitraniline show that benzamide, and hydroxamic acids yield deep red dyes. Iodo compounds produce red colour but the dye could not be isolated. Expreiments with Cl-, Br- compounds gave inconsistent results.

COOH has the same grouping as $CONH_2$ and should be capable of coupling. Unfortunately however, diazo compounds couple best in alkaline solution when carboxyl group is present in the form of the resonating structure $C{<}^{O}_{O}$ }—Consequently the resonance hybrid possesses less energy than can be assigned on the basis of the similarity with $CONH_2$ group. Consequently coupling of this group should be difficult. It may, however, be possible where a very strongly coupling diazonium compound acts on the acid under conditions where activation energy is available ; *e.g.* when trinitrobenzene diazonium chloride acts upon benzoic acid in the presence of actinic rays which can be absorbed by COOH group.

$C = S(OH)$, $C =$ (SH) groups do not suffer from the same defect to an equal extent and hence the coupling of these compounds should be easier.

Iminoethers because they possess the same structure which can relay the lone pair through the conjugated system to the *ortho* and *para* positions should be capable of coupling with diazo/ compounds. Thus $C_6H_5 — C — NH(OEt)$ should couple.

Diazotisation.—Of all the substances aromatic amines are found to diazotise the most easily. This can only be due to the electronic character of the phenyl group attached to the amino group. The electronic character of phenyl groups is quite similar to that of the acyl groups. Thus both aniline and acetamide are weak acids as well as weak bases Therefore benzamide and other amides should be capable of diazotisation.

The stability of diazonium salts is attributed to the resonance between the structures
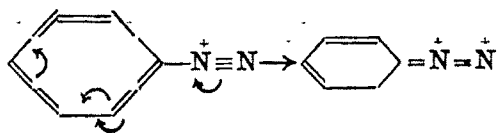
Similarly acyl amides can have the resonating structure
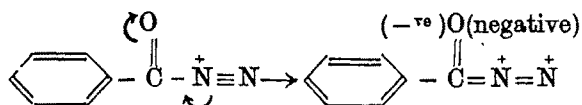
Hence the conclusion can be drawn that acyl amides should prove capable of being diazotised and then coupled to phenols. It is known that just as negatively substituted anilines are with difficulty acted upon by nitrous acid, and the diazonium salts give the corresponding phenols with difficulty, similarly the negatively substituted amides show great reluctance in parting with their NH_2 group. In fact the formation of an intermediate stable diazocompound has been postulated e.g. in the case of $(C_6H_5)C_3CONH_2$ (triphenyl acetamide). Preliminary experiments with benzamide indicate the formation of an azo compound which is not stable.

Work on both the theoretical and practical aspects of the electronic theory is proceeding in these laboratories. Further results of this theoretical approach will be communicated shortly. Experimental verifications of these predictions will be communicated separately when quantitative data are complete.

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THE MAGNETIC STUDY OF PERIODATES. PART I
THE STRUCTURE OF PERIODIC ACID

By SUNDER LAL AGGARWAL AND SURJIT SINGH

Magnetic susceptibility of periodic acid has been determined both in the solid state as well as in solution. The values tally with each other quite well. From this the acid appears to exist both in the solid state as well as in solution as $HIO_4, 2H_2O$.

The metallic periodates correspond to a number of periodic acids but H_5IO_6 is the only one known in the solid state. This may either be regarded as metaperiodic acid dihydrate, $HIO_4, 2H_2O$, or as paraperiodic acid, H_5IO_6 (Mellor, "Treatise on Inorganic and Theoretical Chemistry," Vol. II, p. 386). The acid on dehydration at low pressure yields HIO_4 which accords with its formulation as $HIO_4, 2H_2O$ (Lamb, *Amer. Chem. J.*, 1902, **27**, 134; Partington and Bahl, *J. Chem. Soc.*, 1934, 1088). The polybasic character of the acid however favours the formula H_5IO_6 (Rosenheim and Lowanthal, *Kolloid Z.*, 1919, **25**, 53; Giolitti, *Gazzetta*, 1902, **32**, 340; Ostwald, *J. frat. Chem.*, 1885, **32**, 311).

We have determined the magnetic susceptibilities of the periodic acid in the solid state and in solutions of different concentrations with a view to ascertaining its constitution.

EXPERIMENTAL

Secondary Sodium Paraperiodate.—$Na_2H_3IO_6$ was prepared by the method of Partington and Bahl (*J. Chem. Soc.* 1934, 1086). (Found: I, 46.21; Na, 16.57; O, 19.8. $Na_2H_3IO_6$ requires I, 46.69; Na, 16.91 per cent and the decomposition $4Na_2H_3IO_6 = 4Na_2O + 2I_2 + 3H_2O + 7O_2$ requires O, 20.58 per cent).

Silver Mesoperiodate.—Ag_3IO_5 was prepared by adding a thin suspension of $Na_2H_3IO_6$ to a boiling solution of silver nitrate (Wells, *Amer. Chem. J.*, 1901, **26**, 278). (Found: Ag, 62·35; O, 15·15. Ag_3IO_5 requires Ag, 61.0 and the decomposition $2Ag_3IO_5 = AgI + 4Ag + 5O_2$ requires O, 14.87 per cent).

Periodic acid was prepared by suspending silver mesoperiodate in water and passing a current of chlorine in it until the whole of black silver periodate was converted into silver chloride. The filtrate from AgCl was concentrated upon a water-bath at 60—70° which on keeping in vacuum desiccator over $CaCl_2$ deposited monoclinic crystals of periodic acid. The solid after crystallisation and drying over P_2O_5 gave I, 55.10%; O, 24.7; H_5IO_6 requires I, 55.7 per cent and the decomposition $4H_5IO_6 = 10H_2O + 2I_2 + 7O_2$ requires O, 24.51 per cent).

Potassium metaperiodate was prepared as by Bahl and Surjit Singh (*J. Indian Chem. Soc.*, 1940, **17**, 167).

Susceptibility determinations.—The susceptibilities were measured by the modified Guoy's method (Negvi, *Current Sci.*, 1935). Conductivity water ($\chi_M = -0.722 \times 10^{-6}$) was used as the reference substance. Determinations on compounds of known susceptibilities are reported in Table I. The maximum difference is within 0.3%.

TABLE I

Substance.	Mean of three observations.	Reported value (Inter. Crit. Tables).	Deviation.
	$-\chi m/g.$		
Potassium chloride	0.515×10^{-6}	0.516×10^{-6}	0.2%
Naphthalene	0.718	0.717	0.2
Ethyl alcohol (34°)	0.744	0.744	0.0
Camphoric anhydride	0.622	0.620	0.3
1 : 3 : 5-Trinitrobenzene	0.351	0.352	0.3

The susceptibilities of potassium metaperiodate, sodium paraperiodate and periodic acid in the solid state are given in Table II. The susceptibilities of the solutions of the acid are tabulated in Table III along with calculated values of susceptibility of the solute from the relation,

$$\chi_{Solution} = \chi_{Solute} \cdot C_s + (I - C_s) \chi \text{ solvent}$$

C_s is the weight of the solute per g. of the solution.

TABLE II

Substance.	$-\chi m/g$	$-\chi m/g$ mol.
Potassium metaperiodate (KIO_4)	0.303×10^{-6}	66.7×10^{-6}
Sodium paraperiodate ($Na_2H_3IO_6$)	0.261	70.29
Periodic acid (H_5IO_6 or HIO_4, $2H_2O$)	0.313	71.36

TABLE III

Conc.	Density.	C_s	$-\chi_m \times 10^6$ of soln.	$-\chi \times 10^6$ of solute.	$-\chi \times 10^6$ per g. mol. of solute.
1.701N	1.285	0.3018	0.5947	0.305	69.50
1.392	1.234	0.2578	0.6109	0.297	67.44
1.121	1.189	0.2149	0.6346	0.322	73.45
0.804	1.134	0.1616	0.6543	0.314	71.53
0.705	1.116	0.1441	0.6609	0.310	70.58

Mean—70.5

DISCUSSION

The molecular susceptibility of a polar salt may be considered as the sum of the susceptibilities of the ions,

$$\chi_m = \chi_{cation} + \chi_{anion}.$$

The ionic susceptibilities have been derived from a number of different methods and also from theoretical consideration. Miss Trew reviewed the various methods (*Trans. Faraday Soc.*, 1941, **37**, 476) and gave an average set of values for ionic susceptibilities derived from experimental results. The average ionic susceptibilities for Na and K ions are -6.8×10^{-6} and -14.9×10^{-6} in most of their salts. Hydrogen ion is generally considered to have zero ionic susceptibility in the solid acids.

The molecular susceptibilities of H_5IO_6 and HIO_4 can therefore be calculated from the χ_M values of $Na_2H_3IO_6$ and KIO_4 by subtracting for two Na^+ ions and one K^+ ion respectively. The values so calculated come to be -56.69×10^{-6} for H_5IO_6 and -51.8×10^{-6} for HIO_4. This calculated value for H_5IO_6 is very much divergent from the experimental χ_M of periodic acid (Table II). The periodic acid therefore does not possess the structure H_5IO_6. On similar lines the χ_M for HIO_4, $2H_2O$ can be calculated, by summing the above calculated values of χ_M HIO_4 (-51.8×10^{-6}) and χ_M of two molecules of water ($1 \times -12.96 \times 10^{-6}$). This works out to be -77.72×10^{-6}. Taking into account the depression in diamagnetism due to existence of water molecules as water of hydration, this calculated value of HIO_4, $2H_2O$ is in good agreement with the experimental value of -71.36×10^{-6} (Table III). The χ_M of the acid both in the solid and in its solutions is equal within experimental error. Thus 'periodic acid both in the solid state and in its solutions exists as HIO_4, $2H_2O$.

HYSTERISIS IN THE SOL-GEL TRANSFORMATIONS OF AGAR

By S. N. BANERJI

The phenomenon of hysterisis in the sol-gel transformations of agar sols have been studied under different conditions. A tentative theory based upon the assumption of orientation of the colloidal particles to form a structure has been presented.

It has been shown in a previous paper (Banerji and Ghosh, *Proc. Nat. Acad. Sci., India*, 1939, **9**, 148) that the change in the viscosity of agar sol with age is very slow. It has been concluded from these results that the aggregation tendency of agar particles and hence their orientation originating from a " loose crystallographic force " is a very slow process. From a study on the phenomenon of hysterisis on the sol-gel transformations of reversible sols like those of gelatin and soap (*Z. anorg. Chem.*, 1930, **194**, 305) it has been pointed out that a difference in the melting and setting points of such gels or sols exists due to a slow process of orientation of the colloidal particles. In the present communication the phenomenon of hysterisis in the sol-gel transformations of agar sols has been studied under different conditions. The experimental details are the same as followed in the case of gelatin and soap sols (*cf.* Banerji and Ghosh, *loc. cit.*). The experimental results with agar sols are given below.

TABLE I

Melting		Setting		Melting		Setting	
Temp.	Time	Temp.	Time	Temp.	Time	Temp.	Time
Sol=1.5 g. in 100 c.c.				Sol=2.0 g. in 100 c.c.			
75°	1 min	27	11 min	80	1	27	8
70	1.5	30	19	75	1.5	30	15
65	3	35	45	70	2.5	35	40
60	15	—	—	65	21	—	—
55	30	—	—	60	30	—	—
Sol=2.5 g. in 100 c.c.				Sol=3.0 g. in 100 c.c.			
80	1.5	27	4	78	3.5	29	3
75	2.0	30	8	75	6	32	5
70	3.0	35	32	70	10	35	9
65	29	—	—			38	16
60	35	—	—	65	34	40	30
				60	40	—	—
Sol=4.0 g. in 100 c.c.							
78	4.5	30	2				
75	8.0	32	3.5				
70	18	35	6.5				
65	30	37	11				
		40	28				

If these results on the melting and setting points of agar gels and sols are plotted it is found that the differences in melting and setting points or the hysterisis in degree centigrades for 12 minutes of observation for different concentrations of agar sols are as follows :—

TABLE II

Conc. agar sol (%)	1.5	2	2.5	3	4
Hysterisis for 12 min.	33.5	38	38	31.5	35

The hysterisis in sol-gel transformations of agar first increases and then decreases, passes through a minimum and finally increases with the increasing concentrations of agar. This result is similar to that obtained previously with soap and gelatin sols An explanation based on orientation of colloid particles and subsequent aggregation has been already developed.

Thus with an agar sol of 4% concentration, the difference between the melting and setting points for 12 minutes of observation is as high as 35° (cf. 4·5° with a 10% gelatin sol for the same period). It will be interesting to note that the viscosity change of an agar sol with time is also very slow in comparison to those observed in the case of a gelatin sol. It can therefore be concluded that in the case of reversible sols like soap, galatin and agar, the slower the increase in the viscosity of these sols with age, the greater is the degree of hysterisis in the sol-gel transformations. It has also been shown in the sol-gel transformations of other substances that hysterisis is considerably lowered by sowing a sol with already formed gel of the same concentration as this hastens the process of orientation. The results of similar experiments on agar sols have been shown below.

TABLE III

AGAR SOL CONC.—2%

Melting		Setting					
		Ordinary		Sown with gel		With stirring	
Temp.	Time.	Temp.	Time.	Temp.	Time.	Temp.	Time.
80	0.1 min.	27	8 min	27	5 min.	27	6 min.
75	·1.5	30	15	30	11	30	13
70	2.5	35	40	35	29	35	30
65	21	—	—	—	—	—	—
60	35	—	—	—	—	—	—

If the time-temperature curve is plotted it is seen that the amount of hysterisis of 2% sol for twelve minutes diminishes from 39° to 34° on sowing and 35° on stirring.

It appears from these observations that the formation of a gel or separation of thick gelatinous precipitate in the cases of sol-gel transformation resembles to some extent the separation of solid from a supersaturated solution. When a sol is gradually cooled, more and more of aggregated molecules and colloid micelle appear and are in an oriented condition. The orientation is caused by a similar kind of force which causes crystallisation, but

the particles both of molecular and colloidal dimension are unable to form coarse aggregation because they are protected by a layer of water present on the surface of these particles. The experimental results on the gelation of agar sols show that previous inoculation of sols with gels of the same concentration and temperature hastens the process of gelation and hence this has a close resemblance to the separation of a solid from a supersaturated solution.

Bradford (*Biochem. J.*, 1920, **14**, 91) points out that the formation of a gel by cooling a sol is a case of crystallisation from a supersaturated solution. Moller (*Kolloid Z.*, 1919, **67**, 25) likewise believes gelatinisation to be a kind of crystallisation in which a lattice is formed that entrains some liquid within it, and Von Weimern (*Z. Chem. Ind. Koll.*, 1912, **11**, 239) concludes from his investigations that a jelly is a sponge composed of highly disposed crystallised granules soaked in a dispersive medium. It may be of interest to recall here that the process of sol-gel transformation is a continuous process and there is no evidence to show that aggregation of colloid particles or of heavy molecules present in the gelatin, soap or agar sol, is suddenly rapid when a gel separates out. Thus Walpole (*Kolloid Z.*, 1913, **13**, 241) showed that the refractive index changed slowly but continuously as a gelatin sol was allowed to gelate. Also, it has been observed here that when 1% agar sol is allowed to gelatinise slowly at a temperature of 29·5°, the change in the extinction coefficient as observed with a Nutting's Spectrophotometer in the region, 6000 Å is extremely slow and is practically constant (Table IV).

TABLE IV

Agar sol conc. = 1%   Temp. = 29.5°

Condition	Time	Extnc. coeff.
Sol.	5 min.	0.12
,,	20	0.12
,,	35	0.12
Gel.	50	0.12

From these results it is concluded that there is practically no change in the number, size or structure of colloid particles during the course of the setting of agar sol because the amount of light transmitted does not differ.

It is well known that there exists a considerable disagreement as to the structure and phase of a gel system. Katz (*Koll.-Chem. Beih.*, 1917, **9**, 1) discusses a gel as a homogeneous phase whilst several investigators consider a gel as made up of two phases. Ultramicroscopic study beginning with the work of Zsigmondy (*Z. aonrg. Chem.*, 1911, **71**, 356) has shown that many gels are apparently without structure and in some cases, a structure is seen where fibrils join and intersect as long straight threads. McBain and co-workers (*Proc. Roy. Soc.*, 1921, **98**, A, 395) report such structure in the case of soap gels, whilst Barret (*Biochem. J.*, 1920, **14**, 198) has shown the existence of fibrils in the case of fibrinogen.

It has already been pointed out that the process of the separation of gel from a sol is not a sudden process and gelation of sols like agar, gelatin or soap is continuous. It has also been shown that there is an orientation of colloid particles in the sol state and the sols may show a distinct rigidity. This orientation of colloid particles, which imparts a rigidity rapidly increases with the lowering of temperature and with time.

It is, therefore, suggested that at the moment when a gel is formed from a sol, the orientation of colloidal micelle has reached the highest value to attain the rigidity which characterises a solid body from the condition of a liquid. When, therefore, the 1% sol of agar is kept at a temperature of 30°, the number of colloidal micellae is not increasing with increasing time but they are gradually arranging themselves to an oriented form. This orientation is a very slow process because of the slow diffusion of the dispersed particles. When finally sufficient orientation has been reached the sol appears as a gel, where the aggregation of the dispersed agar particles is not much different from that in the sol condition. The coarsening is stopped as has already been pointed out, by the hydration of the colloidal micelle. When however the gel is kept for a sufficiently long time, the colloid particles gradually lose the affinity for water, get dehydrated and aggregation occurs and finally the phenomenon of syneresis is observable. It is well known that substances lose their adsorptive capacity with time. It is therefore suggested that in those cases where an evidence of the structure of a gel has been obtained from ultramicroscopic observations, the colloid particles have lost some of the protecting layer of water and their aggregation has set in.

It may be of interest to mention here that Schalek and Szegvary (*Kolloid, Z.*, 1923, **33,** 326) studied the effect of shaking on the concentrated and aged sols of ferric hydroxide. These sols set to a gel on addition of an electrolyte of suitable concentration, the gels on shaking become less viscous and mobile again and the sols thus formed gelate again, the whole process being capable of repetition. They have measured the viscosity change during gelation and have followed the process of the changes by an ultramicroscope. They show that in the course of gelation the particles do not meet each other. Their results greatly support the views developed here for the process of gelation from a sol.

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SYNTHETICAL INVESTIGATIONS ON PODOCARPIC ACID*

By Bidyut Kamal Bhattacharyya

The reaction between ethyl 12 : 6-dimethyl*cyclo*hexanone-6-carboxylate and the Grignard complex obtained from β-(p-methoxyphenyl)-ethyl chloride furnishes 1-(β-p-methoxyphenylethyl)2 : 6-dimethyl-6-carbethoxy*cyclo*hex-1-ene which on cyclisation followed by hydrolysis and demethylation yields 1 : 2-dimethyl-6-hydroxy-1 : 2 : 3 : 4 : 9 : 10:11 :12-octahydrophenanthrene-1-carboxylic acid.

Sherwood and Short (*J. Chem. Soc.*, 1938, 1006) have investigated the resin acid—podocarpic acid—isolated from the resin of *podocarpus cupressinus* (Oudemans, *Ber.*, 1873, 6, 1122 ; *Annalen* 1873, 170, 214) and suggested the formula (I) as the probable structure on the basis of the evidence that 6-hydroxy-1-methylphenanthrene is obtained in good yield by dehydrogenation of the acid and that the carboxyl group of it is much more highly hindered than that of the other resin acids. Recently, however, Campbell and Todd (*J. Amer. Chem. Soc.*, 1942, 64, 928) by a series of elegant degradative reactions have conclusively proved that podocarpic acid is correctly represented by the formula (II, $R_1 = R_2 = H$).

(I)   (II)
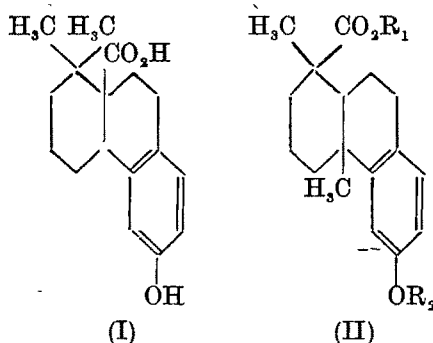
In our attempt for the synthesis of podocarpic acid by the method which has been modelled after those of Howarth and Barker (*J. Chem. Soc.*, 1939, 1299), though we have been successful in building up its structure, the isolation of any of the four possible stereoisomers in the pure state remains yet to be accomplished.

p-Methoxy-phenylethyl alcohol is converted into the corresponding chloride by means of thionyl chloride and dimethylaniline. The Grignard complex, obtained from the above chloride, has been made to react with ethyl 2 : 6-dimethyl*cyclo*hexan-1-one-6-carboxylate in benzene solution to yield a mixture of the unsaturated and the hydroxy compounds (III and IV) together with the product (V, R=CH₃) formed by Wurtz reaction. The above mixture of (III) and (IV) is dehydrated by heating with potassium hydrogen sulphate at 180° for two hours, when pure (III) is obtained. The ring-closure with usual reagents *e.g.*, anhydrous aluminium chloride, 85 per cent sulphuric acid and syrupy phosphoric acid is not at all promising. The above compound (III) when refluxed with a

mixture of acetic and sulphuric acids for one hour, yields (II, $R_1=C_2H_5$; $R_2=CH_3$) ; refluxing for about two hours produces considerable amount of tarry matter. The above cyclised product is hydrolysed in the crude state with 20 per cent methanolic caustic potash to yield (II, $R_1=H$; $R_2=CH_3$). The ethyl ester of the above acid is obtained by the usual alcohol-sulphuric acid method.

In order to dehydrogenate the above octahydrophenanthrene derivative it is heated with selenium at 300° when the acid sublimes unchanged. Therefore the acid is esterified with diazomethane to give the solid methyl ester (II, $R_1=R_2=CH_3$) whose ultra-violet absorption spectrum closely resembles that of the methoxymethyl ester of natural podocarpic acid (Sherwood and Short, loc. cit.). On demethylation of the acid (II, $R_1=H$; $R_2=CH_3$) by refluxing with a mixture of 48 per cent hydrobromic and glacial acetic acids the corresponding phenolic acid is obtained, but it does not give any colouration with alcoholic ferric chloride. Incidentally it may be mentioned that (V) on demethylation also fails to give the ferric chloride colouration.

(IV)   (III)   (V)
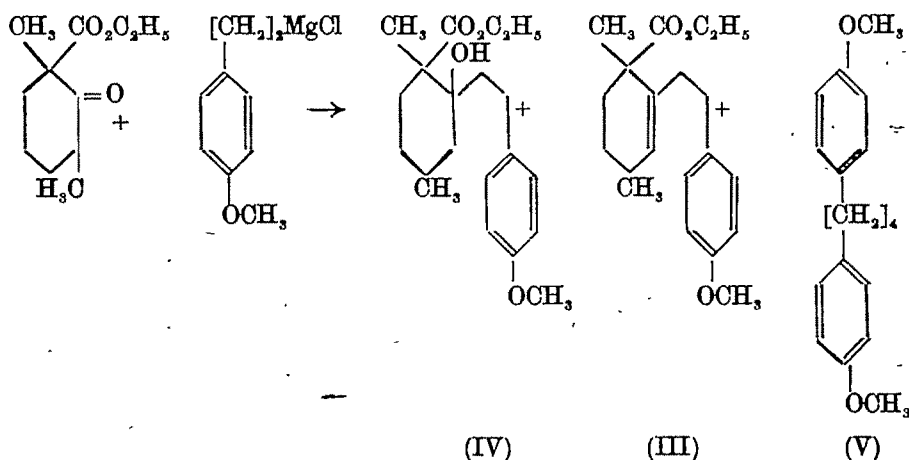
EXPERIMENTAL

Ethyl 2:6-Dimethylcyclohexanone-2-carboxylate.—Ethyl 2-methylcyclohexanone-2-carboxylate (60 g.) was refluxed on the water-bath for 2 hours with sodium (0.6 g.) and alcohol (45 c.c.) to yield the corresponding pimelic ester derivative (65 g.). The Dieckmann reaction with two atoms of sodium in benzene gave only a 45-50 per cent yield of the cyclic compound which was next methylated in benzne.

p-Methoxyphenylethyl alcohol.—The following method furnished a better yield than that used by Short, Plimmer and Hill (*J. Chem. Soc.*, 1938, 694).

A mixture of magnesium (13 g.), ether (50 c.c.) and methyl iodide (1 c.c.) was refluxed and when the reaction started, a solution of p-bromo-anisole (72 g.) in ether (200 c.c.) was dropped slowly during 5 hours ; the vigour of the reaction was maintained all the time. After the reaction was complete, the solution was cooled in ice and then a cold solution of ethylene oxide (26 g.), prepared from ethylene chlorohydrin and powdered caustic potash, in benzene was dropped into the solution of the Grignard complex in two lots.

During the addition the flask was constantly shaken as the yield depended on efficient cooling. The reaction mixture was allowed to stand for three days and then heated on the water-bath for 2 hours. It was worked up in the usual manner ; yield over 73%.

p-Methoxyphenylethyl Chloride.—Thionyl chloride (21 c.c.) was added to a cooled solution of the above alcohol (39.5 g.) in dimethylaniline (31 g.). The solution was allowed to stand for 12 hours and then heated on the water-bath for 1 hour. It was worked up in the usual way ; yield 40.5 g. The use of pyridine in place of dimethyl-aniline does not give any consistent result.

Mixture of unsaturated and hydroxy compounds (III and IV).—Magnesium (7 g.) was covered with ether (100 c.c.) and the ether was refluxed. A solution of methyl iodide (1 c.c.) in ether (10 c.c.) was then added when the reaction set in. After the vigour of the reaction subsided somewhat a solution of the *p*-methoxyphenylethyl chloride (12 g.) in ether (30 c.c.) was added slowly during $3\frac{1}{2}$ hours. After completion of the reaction it was cooled in ice and a solution of ethyl 2 : 6-dimethyl*cyclo*hexanone-6-carbo-xylate (30 g.) in ether (30 c.c.) was then added to it. The reaction mixture was left over-night and heated on the water-bath to drive away most of the ether. Then benzene (25 c.c.) was added and the refluxing was continued for $1\frac{1}{2}$ hours. The reaction product was decomposed with iced dilute sulphuric acid, extracted with ether and dis-tilled, b p. 180-200°/3 mm. [Found : C, 74.85 ; H, 8.6 indicating that the substance is a mixture of (III) and (IV)].

1-(β-*p-Methoxyphenylethyl*)-2 : 6-*dimethyl* - 6 - *carbethoxycyclohex - 1 - ene.*—The dehy-dration was carried out with the crude mixture of (III and IV) obtained after distilling the lower boiling fraction (b.p. 100-140°/8 mm.) ; The mixture of (III) and (IV) (3 g.) together with anhydrous potassium hydrogen sulphate (6 g.) was heated in an oil-bath for 2 hours at 180°. The mixture was extracted with ether and distilled, b.p. 180°/3.5 mm. yield 2 g. ; $[n]_D^{26}$, 1.5266. (Found : C, 76.85 ; H, 8.54. $C_{20}H_{28}O_3$ requires C, 75.95 ; H, 8.86 per cent).

1 : 12 - *Dimethyl - 6 - methoxy* - 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12 - *octahydrophenanthrene - 1 - carboxylic Acid.*—The above unsaturated ester (3 g.) was boiled with a mixture of glacial acetic (27 c.c.) and sulphuric (3 c.c., *d*, 1.84) acids for 1 hour. The solution was diluted with water and the precipitated oil extracted with ether. The ether was distilled off and the residue hydrolysed with methanolic caustic potash (20 per cent, 30 c.c.) by re-fluxing for 30 hours. The methanol was driven away and the residue diluted with water and extracted with ether. The alkaline solution was acidified with iced dilute sulphuric acid and extracted with ether. On removal of ether, the residue was taken in acetic acid solution when after standing for 2 days crystals were deposited. The crude acid was dissolved in methanol, charcoaled and filtered, m.p. 196-7° ; yield 0.01 g. (Found : C, 74.94 ; H, 8.08. $C_{18}H_{24}O_3$ requires C, 75.0 ; H, 8.33 per cent).

The above crude acid was esterfiied as usual and distilled, b.p. 170°/3 mm., $[n]_D$, 1.5120.

1 : 12 - *Dimethyl - 6 - hydroxy* - 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12 - *octahydrophenanthrene - 1 - carboxylic Acid.*—The above acid (0.1 g.) was refluxed with a mixture of hydrobromic (48%

2 c.c.) and acetic (5 c.c.) acids for 7 hours. On cooling crystals were deposited. It was crystallised from dilute methanol, m.p. 258-60°. (Found : C, 74.1 ; H, 8.1. $C_{17}H_{22}O_3$ requires C, 74.45 ; H, 8.0 per cent).

1 : 4 - *Di - (p - methoxyphenyl) - butane.*—The Wurtz's reaction product in the above Grignard reaction was crystallised from petroleum ether (b.p. 40-60°) in plates, m.p. 83°. (Found : C, 80.48 ; H, 8.26. $C_{18}H_{22}O_2$ requires C, 80.0 ; H, 8.14 per cent). It was demethylated in the above way and crystallised from methanol, m.p. 156°. (Found : C, 79.23 ; H, 7.4. $C_{16}H_{18}O_2$ requires C, 79.34 ; H, 7.45 per cent).

Methyl 1 : 12-*Dimethyl*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthrene*-1-*carboxylate.*—The acid (II, $R_1=H$; $R_2=CH_3$; 0.2 g.) in ethereal solution was treated with diazomethane. It was allowed to stand for 4 days. The excess of diazomethane was destroyed with acetic acid and ethereal layer was washed with dilute alkali and water. On removal of ether a solid separated which was crystallised from dilute methanol, m.p. 136-137.5°. (Found : C, 74.0 ; H, 9.1. $C_{19}H_{26}O_2$ requires C, 74.1 ; H, 9.2 per cent).

The ultraviolet absorption curve of the ester in methanol is shown below.
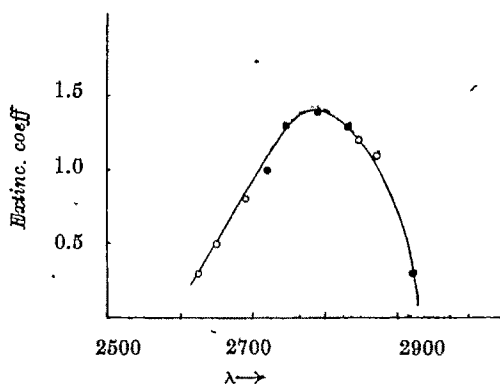
My best thanks are due to Prof. P. C. Mitter for his valuable advice and encouragement during the course of this investigation. My thanks are also due to Messrs. G. Karmakar, M.Sc., B. M. Bisui, M.Sc. and N. Ghosh, M.Sc. for the ultraviolet absorption spectrum, the measurement of refractive indices and microanalysis of some of the compounds respectively.

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ON THE PREPARATION OF IODO-CHLORO-OXYQUINOLINE

By M. K. Bose

A new method is described for the preparation of 5-chloro-7-iodo-8-hydroxyquinoline.

5-Chloro-7-iodo-8-hydroxyquinoline, first introduced as odourless iodoform, has come to stay as an internal antiseptic for amoebic infection (Leake, *J. Amer. Med. Assoc.*, **98**, 195 ; David *et al.*, *ibid.*, **100**, 1658). A survey of the literature did not reveal any method for its preparation excepting one or two patented processes dealing mainly with one or other of the intermediate compounds used in the preparation, or describing a process that could be used in the preparation of such intermediates, (B. P., 3915 ; Ghosh and others, *J. Indian Chem. Soc.*, 1944, **21**, 354). The present process starts with acetanilide which is chlorinated to *p*-chloroacetanilide (Orton, *J. Chem. Soc.*, 1899, **75**, 1050) from which in turn is prepared 4-chloro-2-nitrophenol in two ways : (*i*) *p*-chloroacetanilide is nitrated to 4-chloro-2-nitroacetanilide which on hydrolysis with a concentrated solution of sodium hydroxide is directly oxidised to 4-chloro-2-nitrophenol. Evidently the presence of the NO$_2$ group in the *ortho* position to the amino group in 4-chloro-2-nitro-acetanilide facilitates the oxidation ; (*ii*) *p*-chloroacetanilide is hydrolised to *p*-chloroaniline with sulphuric acid and the solution after diazotisation in the usual way is poured into dilute nitric acid. On decomposition of the diazo solution on the water-bath, good yields of 4-chloro-2-nitrophenol are obtained. Only one molecule of nitric acid is necessary for one molecule of *p*-chloroacetanilide and isolation of intermediate products is unnecessary. This reaction of decomposition of diazo compounds in presence of nitric acid is being studied for the preparation of other important nitrophenols.

For the preparation of 5-chloro-8-hydroxyquinoline, the use of the corresponding amine for the Skraup's reaction could be dispensed with as in other well known industrial processes (Alizarin Blue from Alizarin Orange etc.). Ghosh and others (*loc. cit.*) have prepared 5-chloro-8-hydroxyquinoline from 4-chloro-2-nitrophenol using only sulphuric acid and glycerine but it is found practically impossible to control the reaction particularly when tackling large quantities of the nitrophenol. The addition of acetic acid (Cohn and Gustavson, *J. Amer. Chem. Soc.*, 1928, **50**, 2709) to the reaction mixture not only makes the reaction smooth but also greatly improves the yield. The iodination of the chlorohydroxyquinoline is effected by the addition of dilute acid to a mixture of a solution of the base and iodine in alkali. The base is usually dissolved in potassium hydroxide and iodine in sodium hydroxide.

5-Chloro-8-hydroxyquinoline gives insoluble precipitates of definite composition with metals and its applicability as a reagent is being investigated.

EXPERIMENTAL

4-*Chloro-2-nitroacetanilide.*—Use of acetic acid and acetic anhydride as employed by Remmers (*Ber.*, 1874, **7**, 437) for the nitration of *p*-chloroacetanilide was found unnecessary. Nitration was effected as usual with nitric acid in sulphuric acid solution in 85% yield, m.p. 104° (from alcohol).

4-*Chloro-2-nitrophenol*.—(*i*) Crude, moist nitration product from *p*-chloroacetanilide (225 g.) was refluxed in an iron flask with caustic soda (300 g.) in water (600 c.c.) as long as ammonia was evolved (40 hours). The reaction product was transferred into a flask and the red solid residue of the sodium salt of the nitrophenol was dissolved out from the flask with hot water. After cooling, the sodium salt was filtered and dissolved in boiling water, filtered if necessary, cooled somewhat and the nitrophenol precipitated with hydrochloric acid, yield 70% (calculated on *p*-chloroacetanilide) ,m.p. 86° (from alcohol).

(*ii*) *p*-Chloroacetanilide (340 g.) was refluxed with a solution of sulphuric acid (340 c.c., *d* 1.84) and water (1700 c.c.) for 5 hours. After cooling to below 5° a solution of sodium nitrite (140 g.) in water (600 c.c.) was added with stirring and cooling. The diazo solution was next poured into a solution of nitric acid (140 c.c., *d* 1.4) in water (1400 c.c.) in a flask provided with a condenser. After some time the solution was heated on a water-bath and as soon as decompositoin commenced the flask was removed from the water-bath. Evolution of nitrogen gradually became vigorous and eventually subsided. Towards the end, the solution was again heated on the water-bath to complete the reaction. Solid residue in the flask and the condenser was collected the next day and distilled in steam. Pure 4-chloro-2-nitrophenol collected in the receiver, m.p. 86°, yield 60-62% on *p*-chloroacetanilide.

5-*Chloro-8-hydroxyquinoline*.—4-Chloro-2-nitrophenol (450 g.), acetic acid, glycerine and sulphuric acid (*d* 1.84) (900 c.c of each) were taken in a 6 litre flask provided with a condenser and heated in an oil-bath at 150-160° for 8 hours. After cooling, the mass was thoroughly extracted with water and dilute sulphuric acid. The aqueous extract was filtered and nearly neutralised with sodium hydroxide and finally the mineral acid was decomposed with sodium acetate. The solid was collected, dissolved again in sulphuric acid and subjected to distillation in steam to remove traces of 4-chloro-2-nitrophenol. The base was again precipitated as above, filtered and washed, m.p. 123° (alcohol); yield 60% theoretical.

5-*Chloro-7-iodo-8-hydroxyquinoline*.—5 Chloro-8-hydroxyquinoline (300 g.) was dissolved in a solution of potassium hydroxide (110 g.) in water (6 litres). After heating to boiling the solution was filtered and a solution of iodine (350 g.) in sodium hydroxide (150 g.) in water (3 litres) was mixed with the solution of the base. Dilute acetic acid was slowly run in until acid, while the solution was kept thoroughly stirred. After stirring for another hour the mixture was left overnight and the separated solid filtered and washed next day. The solid was again stirred with water while a solution of sodium thiosulphate was gradually dropped in. When excess of iodine was discharged, the solid was filtered, washed with water and finally with alcohol, m.p. of crude product 175°. Crystallised from benzol it melts at 178-79°, yield 90-94%. (Found : Cl, 12.0 ; I, 41.0. Calc. for C_9H_5ONClI : Cl, 11.63 ; I, 41.63 per cent).

PREPARATION OF 5-CHLORO 7-IODO-8-OXYQUINOLINE

By Rabindranath Sen-Gupta

5-Chloro-7-iodo-8-oxyquinoline has been prepared.

Entero-vioform, 5-chloro-7-iodo-8-oxyquinoline, is an extremely useful drug for the treatment of dysentry. Although a number of firms in Calcutta have put up this drug for sale under various trade names, details of its preparation are not available. According to D.R.P. 117, 767, it is prepared by the action of iodine on 5-chloro 8-oxyquinoline and recently Ghosh, Banerjee and Lasker (*J. Indian Chem. Soc.*, 1944, **21**, 455) have described a method of the preparation of the chloro compound starting from 2-nitro-4-chlorophenol by Skraup's reaction.

The present investigation was undertaken in the first instance to prepare the chloro-iodo compound from 8-oxyquinoline which also forms the starting material for the preparation of Yatren and Chinosol, by the action of iodine chloride and iodine trichloride. Unfortunately it has been found that iodine monochloride in acetic acid does not react with 8-oxyquinoline, the unchanged starting material being obtained at the end of the operation. Iodine trichloride, which is recognised to be a strong chlorinating agent, unexpectedly gives rise to 5 : 7-di-iodo-8-oxyquinoline in good yield although a small quantity of the expected chloro-iodo compound may be obtained by dilution of the filtrate after the separation of the di-iodo compound (Lasker and Ghosh, *Science & Culture*, 1944, **10**, 58). Attempts have been made to prepare 5-chloro derivative by the action of chlorine on 8-oxyquinoline. In acetic acid solution, the main product is 5 : 7-dichloro-8-oxyquinoline (*Ber.*, 1892, **21**, 2979). In non-ionising solvents, the chlorination does not proceed to the desired extent as the hydrochloride of the base separates. Attempts have been made to chlorinate the oxyquinoline derivative dissolved in the theoretical quantity of caustic soda so that the hydrochloric acid generated in the reaction would liberate the free base, which being insoluble in water, will be thrown out of solution and thus escape further chlorination. But even in this case the product is 5 : 7-dichloro derivative mixed with unchanged 8-oxyquinoline.

As sulphuryl chloride is known to be an efficient chlorinating agent for phenols, it has been employed in the next series of experiments. In chloroform solution, sulphuryl chloride is found to give a good yield of the monochloro derivative mixed with certain quantity of the dichloro compound. The dichloro compound can be separated easily by evaporating the reaction mixture to dryness and extracting with hot water. The residue gives a m.p. 177° identical with the m.p. of 5 : 7-dichloro-8-oxyquinoline. Contrary to the usual expectation, it is found that the 5-chloro-8-oxyquinoline can be easily obtained from the filtrate by adding sodium acetate and submitting the mixture to steam distillation when the chloro compound passes over smoothly. As sulphuryl chloride can be prepared easily from sulphur dioxide and chlorine, this method of chlorination will prove to be very useful because the same starting material may be used for the preparation of Yatren, Chinsol, Enterovioform and separation by steam distillation will greatly

simplify the process of extracting the desired product as obtained by Skraup's reaction. The iodination of the compound was effected by the method described in D.R.P. 117,767.

EXPERIMENTAL

Preparation of 5-Chloro-8-oxyquinoline.—Sulphuryl chloride (6.7 g.) in chloroform (81g.) was gradually added to the solution of 8-oxyquinoline (7.2 g.) in the same solvent (87 g.) and the solution kept at a temperature 10-15° (time 15-30 minutes). (If the temperature is kept higher the percentage of dichloro derivative is found to be greater). The reaction mixture became warm and fumes of hydrochloric acid were given off. After the reaction was over, the liquid was evaporated to dryness on a water-bath. The residue was boiled with water and filtered. The undissolved residue on crystallisation from acetic acid melts at 177-78° (Hilebrand, *Ber.*, 1888, **21**, 2979). The filtrate was treated with sodium acetate when a greenish yellow precipitate separated. This was filtered off and subjected to distillation with steam when a yellow solid passed over, recrystallised from dilute acetic acid it melts at 125-26°, yield 5 g. (Found : N, 7.67, Calc. for C_9H_6ONCl : N, 7.82 per cent).

It is very soluble in alcohol, chloroform, benzene, less soluble in dilute acetic acid and almost insoluble in water.

5 - Chloro-7-iodo - 8 - oxyquinoline.—5 - Chloro - 8 - oxyquinoline (18 g.) was dissolved in potassium hydroxide (6 g.) and water (400 c.c.) with heating. Potassium iodide (8.3 g.) in water (50 c.c.) was added to the solution of chloro-oxyquinoline. While still warm, the liquid was filtered from insoluble impurities, if any, and cooled to room temperature. To the yellow liquid was added a solution of bleaching powder (142 c.c, 5%) with stirring and the solution allowed to stand overnight. The yellowish brown precipitate was filtered off and washed with water several times. The paste was then rubbed in a mortar with sodium thiosulphate to remove free iodine, filtered and washed with water and finally with hydrochloric acid (1%) to remove unreacted chloro-oxyquinoline. Recrystallised from glacial acid, it was obtained as glistling yellow needles, m.p. 178-79°.

The best thanks of the author are due to Dr. S. C. Niyogy for his help and suggestion.

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THE THERMAL DECOMPOSITION OF SODIUM AND POTASSIUM NITRITES. PART I. STREAMING OF NITROGEN AND CARBON DIOXIDE AND ACTION OF MAGNESIUM OXIDE ON THE FUSEDS NITRITES

By Trambaklal Mohanlal Oza

Experiments have been planned to elucidate the mechanism of the reactions occurring in the decomposition of sodium and potassium nitrites. The primary stage is $2KNO_2 \rightleftharpoons K_2O + NO + NO_2$; this appears to be followed by the action of the nitrogen peroxide on the potassium oxide as $(K_2O + 2NO_2 \rightarrow KNO_2 + KNO_3)$, while nitrogen production appears to result from the action of nitric oxide on the nitrite.

The thermal decomposition of sodium and potassium nitrites has already been studied. Ray (*J. Chem. Soc.*, 1905, **87**, 177) studied the thermal decomposition of sodium nitrite by heating a small quantity in vacuum in two stages : in the first stage, the heating was slow and cautious and nitric oxide and nitrogen (with traces of nitrogen trioxide) were obtained; while in the second stage the heating was much more intense and a reddish brown gas and oxygen were obtained. The reactions were represented by the following equations :

$$3NaNO_2 \rightarrow NaNO_3 + Na_2O + 2NO \qquad \qquad (i)$$

$$4NaNO_2 \rightarrow 2NaNO_3 + Na_2O + NO + \tfrac{1}{2}N_2 \qquad (ii)$$

$$NaNO_3 \rightarrow NaNO_2 + \tfrac{1}{2}O_2 \qquad (iii)$$

$$2NaNO_3 \rightarrow Na_2O + 2NO + \tfrac{3}{2}O_2 \qquad (iv)$$
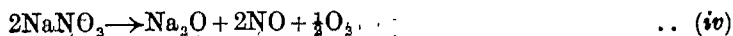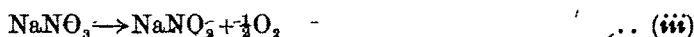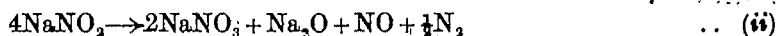
Ostwald (*Annalen*, 1914, **360**, 32) studied the decomposition of alkali nitrites and found that potassium nitrite begins to decompose at 350° according to the following equations :

$$3KNO_2 \rightarrow K_2O + KNO_3 + 2NO \qquad \qquad (i)$$

$$5KNO_2 \rightarrow K_2O + 3KNO_3 + N_2 \qquad \qquad (ii)$$
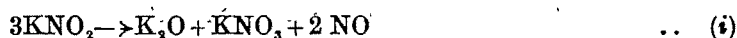
He studied also the action of nitric oxide and nitrogen peroxide upon the dry nitrites and found that the dry salt was not acted upon by nitric oxide so long as the decomposition itself did not occur and that nitrogen peroxide oxidised potassium nitrite to potassium nitrate. He therefore suggested the following additional reactions :

$$NaNO_2 + NO_2 \rightarrow NaNO_3 + NO \qquad \qquad (iii)$$

$$2NaNO_2 + NO_2 \rightarrow 2NaNO_3 + \tfrac{1}{2}N_2 \qquad \qquad (iv)$$
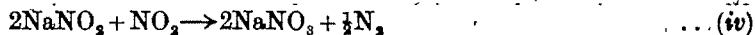
Oza and Shah (*J. Univ. Bom.*, 1942, **9**, 56 ; *J. Indian Chem. Soc.*, 1943, **20**, 261) studied the thermal decomposition of potassium nitrite alone and in presence of charcoal.

They observed that the proportion of nitric oxide was getting steadily smaller and that of nitrogen steadily greater as the reaction progressed or as the mass of the decomposing nitrite was increased and that in presence of charcoal the reaction became violent and soon went to completion. They explained their results on the following equations :

$$2KNO_2 \rightleftharpoons K_2O + NO + NO_2 \qquad\qquad .. \text{ (i)}$$

$$4KNO_2 + 2NO_2 \rightarrow 4KNO_3 + N_2 \qquad\qquad .. \text{ (ii)}$$

$$KNO_2 + NO_2 \rightarrow KNO_3 + NO \qquad\qquad .. \text{ (iii)}$$

$$2KNO_3 \rightarrow 2KNO_2 + O_2 \qquad\qquad .. \text{ (iv)}$$

$$2NO + O_2 \rightarrow 2NO_2 \qquad\qquad .. \text{ (v)}$$
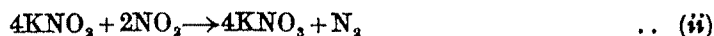
The reversible nature of the initial stage (i) was a suggestion of great importance. Nitrogen was here shown to be formed only by the action of nitrogen peroxide on the nitrite (ii) and nitric oxide by both the direct decomposition (i) and by the reduction of nitrogen peroxide in contact with the nitrite (iii) ; this was thus the same as supposed by Ostwald. Fall in the proportion of nitric oxide and increase in that of nitrogen with progress of the reaction were thus ascribed to the intermediate formation of nitrogen peroxide with oxygen from the nitrate (iv).

Reference may also be made to the work of Mehta (*J. Univ. Bom.*, 1941, **8**, 136), wherein the reactions occurring in the thermal decomposition of nitrites have been summarised as :

$$2MNO_2 \rightleftharpoons M_2O + NO + NO_2 \qquad\qquad .. \text{ (i)}$$

$$M_2O + NO \rightarrow 2M + NO_2 \qquad\qquad .. \text{ (ii)}$$

$$M_2O + 2NO_2 \rightarrow MNO_2 + MNO_3 \qquad\qquad .. \text{ (iii)}$$

$$MNO_2 + NO_3 \rightarrow MNO_3 + NO \qquad\qquad .. \text{ (iv)}$$

$$M + 2NO_2 \rightarrow MNO_3 + NO \qquad\qquad .. \text{ (v)}$$

$$MNO_2 + NO \rightarrow MNO_3 + \tfrac{1}{2}N_2 \qquad\qquad .. \text{ (vi)}$$

$$MNO_3 \rightarrow MNO_2 + \tfrac{1}{2}O_2 \qquad\qquad .. \text{ (vii)}$$
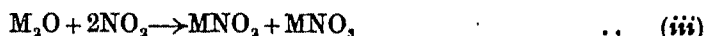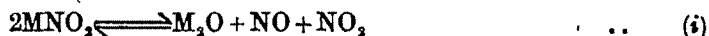
He states that the reactions (i), (iii), (iv), (vi) and (vii) are present in the decomposition of potassium nitrite. The work is not yet thoroughly published and it is therefore not possible to judge the strength of evidence leading to the conclusions. It should be observed that equation (i) of Oza and Shah is indicated in this scheme which brings out in addition, two other points of interest ; namely : (a) the action of nitrogen peroxide on the metallic oxide (iii), and (b) the production of nitrogen from nitric oxide in contact with the nitrite (vi) and *not* directly from nitrogen peroxide [(ii) of Oza and Shah]. It will thus be seen that the mode of production of nitrogen requires clearer elucidation.

The present work arose from the observation of Oza and Walawalker (*J. Indian Chem. Soc.*, 1943, **20**, 315) that pure potassium nitrite melted with decomposition. It was therefore thought that the products of the initial stage in the decomposition might

be swept out by passing a current of some inert gas (nitrogen) on the nitrite in the fused state and the truth or otherwise of the initial stage can thus be established beyond doubt. Further attempts to isolate larger quantities of the products of the initial stage by generating an inert gas (carbon dioxide) in the inside of the decomposition mass, provided results which afforded considerable insight into the mechanism of reactions resulting in the production of nitrogen. The work thus developed interest and it was thought necessary to check the conclusions by carrying out experiments actually with nitric oxide, oxygen and nitrogen peroxide. Further, since the conditions of the above experiments did not allow of a clear observation into the nature of the residue, experiments were undertaken to provide a reliable information in this direction on the heating of the nitrite, in vacuum, on a platinum surface so that glass on which the potassium oxide, present in the residue attacked spoiling the analytical results, was absent. The results of these investigations are described under Parts I and II.

EXPERIMENTAL

Materials.—Potassium nitrite used was prepared according to Oza and Walawalker (*loc. cit.*). Sodium nitrite was the recrystallized Merck's extra pure substance which gave the following results on analysis :

0.1536 G. substance gave 0.1300 g. NaCl ; 0.0704 g. substance requires 20.4 c.c. 0.1 N-KMnO$_4$. Found : Na, 66.64% ; NO$_2$, 33.27%. Calc. for NaNO$_2$: Na, 66.66%, NO$_2$, 33.33%.

Magnesium carbonate and magnesium oxide were of the extra pure quality of Merck.

Nitrogen was prepared by the action of ammonium chloride solution on sodium nitrite solution. It was bubbled through KOH, alkaline sodium sulphite, acidified ferrous sulphate and ice-cold water and collected over air-free water after letting off about 5 litres. This was then introduced into the evacuated flask (*vide* Fig.) with the aid of a manometer. It was tested for nitric and nitrous oxides which were both found absent.
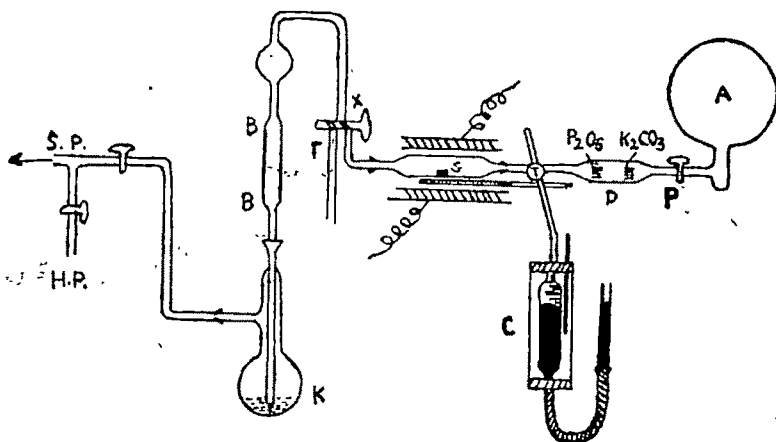
Analysis of the gaseous products and solid residue was carried out as mentioned by Oza and Shah (*loc. cit.*). The oxide could not be estimated by direct titration and, where stated, the figure is calculated from potassium corresponding with the nitrite taken and that corresponding to the nitrite and nitrate present in the residue (found experimentally). Only in experiments with platinum surface (Part II) was the oxide obtained by direct titration with 0.10 N succinic acid. The results of analysis of the solid residue are not to be taken as absolute, as the glass wool with which the substance was packed in the heating tube, made accurate analysis impossible. The results are expected to serve the purpose of broad comparison from experiment to experiment or between different experiments.

Apparatus and Procedure.—The apparatus used is shown in the figure. A weighed quantity of the nitrite was kept at S near a padding of glass wool in an electrically heated tube, the ends of which were connected by ground glass joints to a 3-way tap Q on one side and a 4-way tap T on the other. The tap T was connected to the gas reservoir A through the drying tube D. The third way of T was connected to a measuring burette (surrounded by a water condenser C) to measure, over mercury, the volume of gas passed. The fourth way of T was closed during the course of an experiment : when preparing CO_2 or oxygen, a tube containing $NaHCO_3$ or $KClO_3 + MnO_2$ was sealed on to this, the whole apparatus evacuated and the gas generated by heating the tube collected in A for use during the experiments.* The tap X led to vacuum pumps through an internal seal and a bulb, K, one-third filled with KOH lye. The empty space, BB, allowed the solution in K to rise when making adjustments and F allowed air to be admitted into the system at the end of any experiment. Volume of gas streamed during an experiment was measured off thus : T was closed to the left and the burette kept open to D. By lowering the levelling tube of the burette and opening the tap T gas was drawn into the burette. T was then closed and the burette read off after adjusting levels of mercury. T was then partially opened to the left and gas allowed to bubble as seen in K. When sufficient gas had passed, T was closed to the left, levels of mercury adjusted and the burette read again. The difference between the readings gave the volume of gas streamed.

Before starting an experiment an accurately weighed quantity (1 g.) of the nitrite was introduced at S between plugs of glass wool. All the ground glass joints were fitted up with vacuum grease and the system evacuated and allowed to stand for one day to test for leakage, if any. After adjusting the temperature of the furnace, measured by a mercury-in-silica thermometer (650°) the desired gas was streamed at a practically uniform rate such that about 60 c.c. were passed in about 15 minutes. All experiments were conducted at and near (50° higher) the melting point of the nitrite. The rate of decomposition at these temperatures is negligibly small (Oza and Shah, *loc. cit.*).

Preliminary experiments were carried out with carbon dioxide as streaming gas. The volume streamed was not measured and the experiments were carried out mainly to test the formation of nitrate (diphenylamine test) and oxide in the residue and of nitrate, if any, in the alkali bulb, K. Quite a number of experiments were done and in all, with-

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* In actual practice the gas first filled in A was drawn out by working the hyvac pump. A fresh lot prepared on a second heating was collected for use in the experiments.

out exception, the residue was found to contain oxide and nitrate while the alkali never contained any nitrate. The gaseous products, on the other hand, always contained at least a trace of nitric oxide thus explaining why no nitrate was ever present in the alkali.

The results of experiments with nitrogen as streaming gas are given in Table I. The results showed that (i) N_2O_3 alone and no NO or nitrogen was produced in experiments with $NaNO_2$ though all the three gases were produced with KNO_2; (ii) the solid residue of $NaNO_2$ did not contain nitrate though it contained oxide; (iii) in the case of KNO_2, where both NO and nitrogen were present in gas, production of nitrate also occured in the residue. It thus appeared that nitrogen production was related to nitrate production (vide equations of Ray).

<div align="center">TABLE I</div>

<div align="center"><i>Nitrogen as streaming gas on fused nitrites</i> (1 g.).</div>

Substance.	Temp.	Total gas passed.	Total gas obtained.	Composition of the gas			Compn. of residue		
				N_2O_3.	NO.	N_2.	NO_3. (Na or K)	NO_2. (Na or K)	O. (Na or K)
$NaNO_2$	330°	53.84 c.c.	56.13 c.c.	2.29	Trace	Trace	0.0	0.9884	0.0052
,,	380	60.1	62.65	2.49	,,	,,	0.0	0.9866	0.0061
KNO_2	410	..	65.62	2.63	0.59	,,	0.00825	0.9682	0.0138
,,	460	54.68	61.62	4.73	0.84	0.37	0.0150	0.9470	0.0224

These experiments thus yielded a positive undeniable proof of the initial stage in the decomposition of the nitrites, viz.,

$$2MNO_2 \rightleftharpoons M_2O + NO + NO_2$$
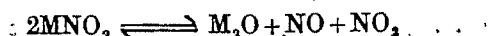
where M is the alkali metal atom. They also showed that the nitrate production was in some way connected with the formation of nitric oxide or nitrogen or both.

The results of experiments with CO_2 as streaming gas are given in Table II and show that (i) nitric oxide, nitrogen and nitrate are all produced with both the nitrites at all temperatures; (ii) the production of oxides of nitrogen is greater with $NaNO_2$ than with KNO_2 and yet the production of nitrogen and of nitrate is uniform in comparable experiments.

<div align="center">TABLE II</div>

<div align="center"><i>Carbon dioxide as streaming gas on fused nitrites</i> (1 g.)</div>

Substance.	Temp.	Total gas passed (N.T.P.)	Total gas obtained (N.T.P.)	Composition of the gas			Compn. of residue	
				N_2O_3.	NO	N_2.	NO_3. (Na or K)	NO_2. (Na or K)
$NaNO_2$	330°	54.38 c.c.	6.06 c.c.	3.4	2.2	0.46	0.0077	0.977
,,	380	55.71	13.32	7.0	5.66	0.66	0.0175	0.947
KNO_2	410	54.71	4.0	2.5	1.0	0.50	0.0095	0.9625
,,	460	54.88	5.7	3.8	1.2	0.70	0.0165	0.9492

These experiments indicated the production of nitric oxide and nitrogen even with $NaNO_2$ at 330° and 380° where in the corresponding experiments with nitrogen (Table I) no nitric oxide and nitrogen are met with. This may be ascribed to the greater effective concentration of the oxides of nitrogen in these experiments than in the others brought about by the displacement of N_2O_3 from the nitrites by CO_2 as :

$$2MNO_2 + CO_2 \longrightarrow M_2CO_3 + N_2O_3.$$
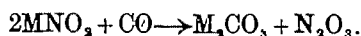
It is seen in the above experiments that the production of nitrate is in some way connected with the production and reduction of oxides of nitrogen. This might occur in any of the ways pointed out in the introduction. Since the production of oxides of nitrogen is but small in all these experiments it was thought that a more correct idea of the operating factors can be had if the oxides of nitrogen could be released in larger amounts. With this end in view it was thought of generating CO_2 within the decomposing mass of the nitrites by admixing the nitrites with some readily decomposable carbonate. An intimate mixture of 0.25 g. nitrite and excess of magnesium carbonate was prepared and put into the heating tube S of the apparatus and the end of the tube projecting out of the furnace (on the side of T) was sealed off. Since $MgCO_3$ decomposed more quickly than at 350° temperature of the furnace was adjusted to that of the experiment as quickly as possible. The results of these experiments are given in Table III. They show that

TABLE III

Heating a mixture of magnesium carbonate and 0.25 g. nitrites

Substance.	Temp.	Total gas evolved (N.T.P.).	Composition of gas			Composition of residue		
			N_2O_3.	NO.	N_2	NO_3. (Na or K)	NO_2. (Na or K)	O. (Na or K)
$NaNO_2$	380°	33.22 c.c.	2.4	29.24	0.58	0.0383	0.1025	0.0487
KNO_2	380	19.25	2.4	17.02	0.33	0.0229	0.133	0.0478
,,	410	22.34	2.8	19.21	0.33	0.0231	0.1222	0.0541
,,	460	17.65	2.3	14.56	0.79	0.02385	0.1355	0.0451

(*i*) nitric oxide and nitrogen peroxide are always present in the gas and the amount of nitrogen trioxide is practically the same in all the experiments ; not only so, it is always smaller than those in experiments of Tables I and II ; (*ii*) the amounts of nitric oxide are far greater than those of nitrogen, the amounts of the latter being negligibly small even at 460° ; (*iii*) the residue (soluble portion) contains both oxide and nitrate together with a practically constant amount of unchanged nitrite.

The results showed without a shadow of doubt that nitrogen was not the primary product of decomposition of the nitrites and that nitrogen production was not directly connected to nitrate production (equations of Ray, *loc. cit.*). The fact that the amounts of N_2O_3 in all these experiments are similar, receives explanation on its steady escape in small amounts during the progress of the reactions. Again the facts that (*i*) the amounts of N_2O_3 in these experiments are much less than what would be expected under the prevailing conditions and (*ii*) the free gas consists of almost all nitric oxide, show that nitrogen

peroxide, produced in the initial stage, is either all used up (fixed up in some way) or reduced to nitric oxide—that this component of the products of the initial stage is more readily reactive than the other. Further, the uniform nature of the gaseous products and of the residues in all these experiments suggests lack of complications in the reactions. The above facts together with the fact that magnesium oxide is present in excess in the residues would suggest that nitrogen peroxide reacts at the instant of its liberation with the magnesium oxide present to form nitrite and nitrate and the former being unstable under the prevailing conditions (Ray, *loc. cit.*) passes into nitrate and nitric oxide forming, at the same time, a little nitrogen (Ray, *loc. cit.*).

These experiments thus suggest that nitrogen peroxide reacts at the instant of its liberation with magnesium oxide present in the residue. In the decomposition of pure nitrites (*i.e.* in absence of magnesium oxide) the product of the decomposition contains alkali oxide—a substance much more reactive to nitrogen peroxide than magnesium oxide. The results therefore lend support to the view (*vide* introduction) that the alkali oxide in the residue reacts with the nitrogen peroxide of the products of the initial stage. This view is corroborated by the results, given in Table IV on heating an intimate mixture of nitrite and magnesium oxide which show (*i*) still smaller production of N_2O_3 than in

TABLE IV

Heating a mixture of magnesium oxide and 0.25 g. of nitrite

Substance.	Temp.	Total gas evolved (N.T.P.).	Composition of gas			Composition of residue		
			N_2O_3.	NO.	N_2.	KNO_3.	KNO_2.	K_2O.
KNO_2	460	27.29 c.c.	1.58	24.87	0.84	0.01305	0.119	0.0645
„	500	23.19	0.94	21.34	0.91	0.02415	0.153	0.0525

the preceding set of results and (*ii*) the same neglibibly small production of nitrogen even when the temperature is raised to 500°.

It is interesting to observe in all the experiments of Tables III and IV that (*i*) nitrogen is present in negligible amounts and (*ii*) nitrite is present in the residues in fairly appreciable amounts and still the reaction, which is very vigorous at the start, becomes considerably slackened in the course of about fifteen minutes though a large excess of magnesium oxide is always present. The latter point could be explained if it is supposed that the nitrite becomes coated with a layer of magnesium nitrate and decomposition of the enclosed nitrite is thus prevented. Such a course would prevent access of nitric oxide to nitrite suggesting that lack of nitrogen production may be due to this cause. In other words, nitrogen production might be occuring by reduction of nitric oxide in contact with the nitrite. Since surface of the nitrite is not exposed to the attack of nitric oxide (it is enclosed by a coating of magnesium nitrate) no nitrogen results. Although there is plenty of nitric oxide in the gas it is in contact with the nitrate and not with the nitrite.

CONCLUSION

The above experiments enable us to draw certain inferences as to the mechanism of reactions occurring in the thermal decomposition of sodium and potassium nitrites. The initial stage in the decomposition is undoubtedly

$$4MNO_2 \rightleftharpoons 2M_2O + 2NO + 2NO_2 \qquad\qquad \ldots (i)$$

the oxides of nitrogen, and not nitrogen itself, being the product of the initial stage.

The nitrogen peroxide and the alkali oxide produced in (i) are likely to react with each other in which case nitrite and nitrate would result as

$$K_2O + 2NO_2 \rightarrow KNO_2 + KNO_3 \qquad\qquad \ldots (ii)$$
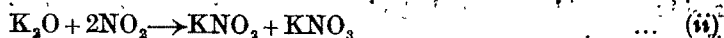
Equation (ii) shows the production of nitrate and disappearance of nitrogen peroxide as found in practice. Equations (i) and (ii) together show also why the residue contains free alkali.

The above study does not enable a definite explanation to be given of the reactions producing nitrogen but makes it likely that it may be the result of the action of nitric oxide on the nitrite. Experiments have been performed to throw light on this point and will be described in Part II.

ORTHO-SUBSTITUTED DIPHENYLS. PART III

BY S. A. FASEEH AND S. H. ZAHEER

o-Phenyl-α : β-dichlorocinnamic acid and *o*-phenyl-ω-chlorostyrene have been prepared. The latter in presence of aluminium chloride has been converted into phenanthrene.

In a preceding paper (*J. Indian Chem. Soc.*, 1944, **21**, 381) the preparation of *o*-phenylcinnamic acid (I) was reported. A detailed study of this interesting compound and some of its important derivatives is being made. On observing the structure of this compound containing the *o*-phenylstyrene residue, it becomes obvious that it would lend itself admirably to a new synthesis of phenanthrene which would have certain advantages over a number of other well known syntheses of this hydrocarbon like those of Pschorr (*Ber.*, 1896, **29**, 496), Bardhan and Sen-Gupta (*J. Chem. Soc.*, 1932, 2520), and Newman and Farbman (*J. Amer. Chem. Soc.*, 1944, **66**, 1550). In all these and similar syntheses of phenanthrene, this hydrocarbon is produced as the result of a drastic pyrogenetic treatment either alone or with zinc or selenium of substituted or hydrogenated intermediate derivatives. The present authors have avoided the use of such pyrogenetic methods and have presented a simple and elegant synthesis of phenanthrene, which clearly indicates the structure of the hydrocarbon and affords an easy method for its preparation and for the preparation of its derivatives

A well powdered suspension of *o*-phenylcinnamic acid in carbon tetrachloride, when saturated with chlorine gas in sunlight, gives the crystalline *o*-phenyl-α : β-dichlorophenylpropionic acid (II). This compound on being boiled with a conncentrated solution of sodium carbonate loses a molecule of carbon dioxide and hydrochloric acid each and yields an oily compound which is the *o*-phenyl-ω-chlorostyrene (III). These reactions and the formation of these derivatives are similar to those studied by Liebermann and Finkenbeiner (*Ber.*, 1895, **28**, 2235) and Biltz (*Annalen*, 1897, **296**, 266) in the case of cinnamic acid.

If the *o*-phenyl-ω-chlorostyrene could be made to condense with the loss of a molecule of hydrochloric acid, involving the closure of the ring at the point of the *O*-hydrogen atom of the second benzene nucleus of the diphenyl it would result in the formation of phenanthrene (IV). This condensation takes place in the presence of aluminium chloride with or without solvent (ligroin). Along with the phenanthrene produced considerable quantities of a brown plastic substance are also obtained whose nature has not yet been closely investigated. Under the best conditions reported below the yield of phenanthrene is nearly 40%.

If this condensation takes place with the removal of hydrochloric acid from the side chain no ring-closure would occur and *o*-diphenylacetylene (V) would be formed. This

(I)   (II)   (III)   (IV)   (V)
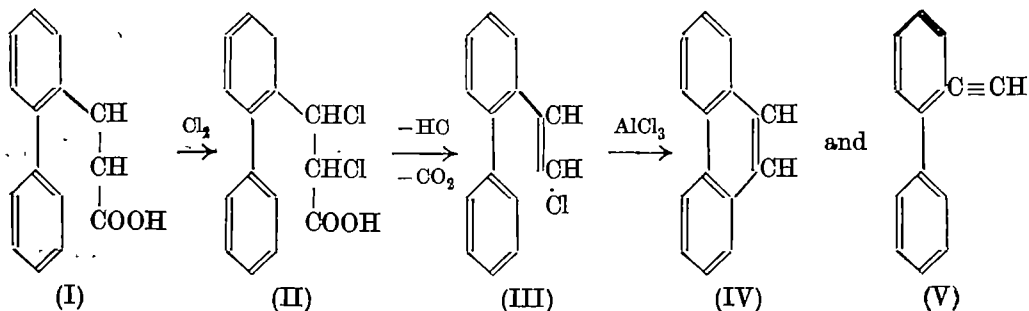
compound has not yet been isolated by us but we suspect that the plastic substance mentioned above is a polymerised product of the acetylene derivative.

EXPERIMENTAL

o-Phenyl-α : β-dichlorocinnamic Acid.—To a suspension of well powdered *o*-phenylcinnamic acid (22.4 g., 1/10 mol) in dry carbon tetrachloride (225 g.) a slow current of dry chlorine was passed in sunlight. The suspension was soon coloured yellowish green. The colour, however, was lost soon on account of the absorption of the dissolved chlorine. The operation was repeated till the colour remained permanent which indicated the presence of an excess of chlorine. During the process of absorption of chlorine a stage was reached when considerable heat was generated, the suspension cleared up and the substance went completely into solution. Very soon after, however, precipitation of granular crystals of a different nature began. The mixture was kept overnight when most of the *o*-phenyl-α : β-dichlorophenylpropionic acid was precipitated. This was filtered off and a further quantity recovered by the removal of carbon tetrachloride by distillation. On recrystallisation from benzene colourless granular cystals were obtained, m.p. 164°; yield 26 g. (88%). (Found : Cl, 23.89. $C_{15}H_{12}O_2Cl_{12}$ requires Cl, 24.04 per cent).

o-Phenyl-ω-chlorostyrene.—*o*-Phenyl-α : β-dichlorocinnamic acid (20 g., 1/15 mol) was dissolved in 100 c.c. of sodium carbonate (7.5 g,, 1/15 mol) solution and heated on the water-bath with a reflux condenser for 7 hours during which time an oil was produced. After cooling the oil was extracted with ether and the ethereal extract dried overnight with anhydrous sodium sulphate. The ether was evaporated off and the residue distilled at 145°/2 mm., yield 13.2 g. (91%). (Found : Cl, 16.41. $C_{14}H_{11}Cl$ requires Cl, 16.55 per cent).

Phenanthrene.—Well powdered anhydrous aluminium chloride (0.19 g,, 1/700 mol) was gradually added to freshly distilled *o*-phenyl-ω-chlorostyrene (4.3 g., 1/50 mol) kept in a small flask fitted with an air condenser, and thoroughly shaken after each addition. The flask was now placed on a water-bath whose temperature was gradually raised to the boiling point, and the contents frequently well shaken. At 42° (bath temperature) a vigorous reaction occurred suddenly with evolution of a large amount of gas and the mixture darkened considerably. The reaction slowed down after about 10 minutes, but the heating was continued for 7 hours on a boiling water-bath till the evolution of hydrochloric acid ceased completely. The dark mass was now treated with ice-cold water and extracted with ether. The ethereal extract was dried over calcium chloride and the ether distilled off. The residue was distilled at 145°/0.5 mm., when the colourless oil solidified into colourless crystals on cooling. The solid on recrystallisation with 70% alcohol gave shining flakes of phenanthrene with a blue fluourescene ,m.p. 99-100°, yield 1.35 g. (38%).

Phenanthrene was converted into its picrate by the usual method. The picrate on being crystallised from redistilled alcohol gave long yellow needles, m.p. 145° (Found : C, 59.15 ; H, 2.95. Calc. for $C_{20}H_{13}O_7N_3$: C, 58.97 ; H, 3.19 per cent). The regenerated phenanthrene had m.p. 99.5° (Found : C, 94.45 ; H, 5.48. Calc. for $C_{14}H_{10}$: C, 94.39 ; H, 5.62 per cent). The identity of phenanthrene and its picrate was confirmed by mixed m.p. with a specimen of pure (Schuchardt) phenanthrene and its picrate.

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ACTION OF p-TOLUENE-SULPHONYL CHLORIDE ON POLYNITRO-OXY-DIPHENYLS

By A. B. Sen

The action of p-toluene-sulphonyl chloride on 3 : 5-dinitro-4-oxydiphenyl and 3 : 5 : 4'-trinitro-4-oxydiphenyl has been examined.

In each case a chloro compound has been obtained in the presence of diethylaniline as the condensing reagent. 3 : 5-Dinitro-4-oxydiphenyl forms also a p-toluene-sulphonate in the presence of sodium carbonate as the condensing reagent.

The action of various amines and amino compounds on these chloro compounds has also been studied.

It is well known that p-toluene-sulphonyl chloride reacts with nitrophenols in two ways (Ullman and Nadai, *Ber.*, 1908, **41**, 1870, 3932 ; Ullman and Bruick, 1909, **42**, 3939 ; Ullman and Sane, *Ber.*, 1911, **44**, 37 ; Sane and Joshi, *J. Chem. Soc.*, 1924, 2481 ; *J. Indian Chem. Soc.*, 1928, **5**, 299 ; Sane, Chakravarty and Pramanick, *ibid.*, 1932, **9**, 55 ; Sane and Joshi, *ibid.*, 1932, **9**, 59 ; 1933, **10**, 459 ; Joshi, *ibid.*, 1933, **10**, 313). Mononitrophenols yield p-toluene-sulphonic esters in the presence of sodium carbonate or diethylaniline as the condensing reagent. Polynitrophenols, specially containing nitro groups in the 2:4 or 2: 6 position to OH, also yield such esters in the presence of sodium carbonate as the condensing reagent, but are converted mainly into polynitro-chlorobenzenes, the OH group being replaced by Cl, in the presence of diethylaniline as the condensing reagent.

The chloro compounds as well as the toluene-sulphonyl esters, obtained from these polynitrophenols, are extremely reactive (Sane and Joshi, *J. Indian Chem. Soc.*, 1932, **9**, 59 ; 1933, **10**, 459). When treated with various amines and amino compounds like aniline, toluidines, pyridine, piperidine, aminophenols, dimethylamine, anisidines, etc., in alcoholic, benzene or toluene solution, they form condensation products.

In the present paper, the above reaction has been extended to 3 : 5-dinitro-4-oxydiphenyl and 3 : 5 : 4'-trinitro-4-oxydiphenyl. In the presence of diethylaniline as the condensing reagent, each of these nitrophenols forms a polynitro-chloro compound. 3 : 5-Dinitro-4-oxydiphenyl yields a p-toleune-sulphonyl ester in the presence of sodium carbonate as the condensing reagent.

The chloro compounds, so obtained, are found to be extremely reactive. They have been treated with various amines and the compounds formed isolated and characterised.

EXPERIMENTAL

3 : 5-Dinitro-4-oxydiphenyl was obtained by the nitration 4-oxydiphenyl in acetic acid solution with nitric acid (d 1.2) according to the method of Garcia Banus (*Chem. Abs.*, 1923, 770), m.p. 154°.

3 : 5-*Dinitrodiphenyl-4-p-toluene sulphonate.*—3 : 5-Dinitrodiphenyl (2.6 g.) and p-toluene-sulphonyl chloride (2 g.) were suspended in about 25 c.c. of hot water in a flask and then solid sodium carbonate was added to it in small quantities. Addition of sodium carbonate each time produced an orange colouration, which disappeared on heating. When the further addition of sodium carbonate did not produce any colouration, the reaction is

complete. The solution was then cooled, and the reaction product formed was filtered and washed with water. It was then recrystallised twice from glacial acetic acid, m.p. 158°, yield 3.4 g. (Found : N, 6.3 ; S, 7.4. $C_{19}H_{14}O_7N_2S$ require N, 6.7 ; S, 7.7 per cent).

3 : 5-*Dinitro-4-chlorodiphenyl.*—3 : 5-Dinitro-4-oxydiphenyl (2.6 g.), *p*-toluene-sul-phonyl chloride (2 g.) and diethylaniline (10 c.c.) were heated together in a flask for 4 hours. The mixture was then cooled and the chloro compound isolated in the usual way. Colourless crystals from alcohol, m.p. 111°, yield 1.5 g. (Found : N, 10.3. $C_{12}H_7O_4N_2Cl$ requires N, 10.1 per cent).

3 : 5 : 4′-*Trinitro-4-oxydiphenyl* was obtained by the further nitration of 3 : 5-dinitro-4-oxydiphenyl in acetic acid solution, with excess of concentrated nitric acid (*d* 1.4) and warming, the solution was then cooled and diluted with water. The solid which separated out was filtered, dried and then recrystallised from toluene, m.p. 205° (Garcia Banus, *loc. cit.*).

In Table I the various compounds obtained from the two chloro compounds are described.

TABLE I

Reactants.	Formulæ of compounds formed.	M.p.	Colour.	% Nitrogen Found.	Calc.
(*i*)	*With 3 : 5-dinitro-4-chlorodiphenyl*				
Aniline	$X.NH.C_6H_5$	165°	Deep scarlet	12.9	12.60
o-Toluidine	$X.NH.C_6H_4.CH_3$	179	Deep orange	12.3	12.03
m-Toluidine	$X.NH.C_6H_4.CH_3$	146	Yellowish orange	12.2	12.03
Dimethylamine	$X.N(CH_3)_2$	94	Orange yellow	14.7	14.60
Piperidine	$X.N.C_5H_{10}$	124	Yellow	12.2	12.70
o-Anisidine	$X.NH.C_6H_4.OCH_3$	188	Red	11.1	11.50
o-Aminophenol	$X.NH.C_6H_4.OH$	170	Brown	11.4	11.90
Ammonia	$X.NH_2$	232	Turmeric yellow	16.4	16.30
(*ii*)	*With 3 : 5 : 4′-trinitro-4-chlorodiphenyl*				
Aniline	$Y.NH.C_6H_5$	199°	Orange yellow	14.2	14.70
o-Toluidine	$Y.NH.C_6H_4.CH_3$	169	Orange	13.7	14.10
m-Toluidine	$Y.NH.C_6H_4.CH_3$	198	Brick red	13.7	14.10
Dimethylamine	$Y.N(CH_3)_2$	159	Yellow	17.4	16.90
Piperidine	$Y.N.C_5H_{10}$	199	Lemon yellow	14.7	15.00
o-Anisidine	$Y.NH.C_6H_4.OCH_3$	212	Red	14.7	14.10
o-Aminophenol	$Y.NH.C_6H_4OH$	208	Red orange	13.6	13.20
Ammonia	$Y.NH_2$	280	Yellow	18.3	18.40

where
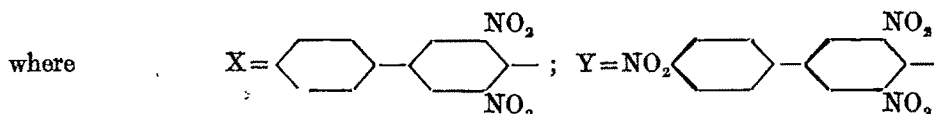
3 : 5 : 4′-*Trinitro-4-chlorodiphenyl.*—3 : 5 : 4′-Trinitro-4-oxydiphenyl (3 g.), *p*-toluene-sulphonyl chloride (2 g.) and diethylaniline (20 c.c.) were heated together in a flask on the

water-bath for 4 hours. The mixture was then cooled, acidified with hydrochloric acid, washed with dilute sodium carbonate and then with water. The chloro compound was then isolated in the usual way and recrystallised twice from acetic acid, m.p. 171°. (Found: N, 12.6. $C_{12}H_6O_6N_3Cl$ requires N, 13.0 per cent)..

Reactivity of the Chloro Compounds.—The calculated quantities of the chloro compound and the amine (slight excess) were dissolved separately in alcohol, benzol or toluol and then mixed and refluxed for $\frac{1}{2}$ hour. The solvent was then distilled off, the excess of amine removed by the addition of concentrated hydrochloric acid and the solid which separated out was washed thoroughly with boiling water and then recrystallised from a suitable solvent (alcohol, benzol or glacial acetic acid).

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VARIATION OF APPARENT MOLAR VOLUME OF NON-ELECTROLYTES IN SOLUTION WITH CONCENTRATION

By W. V. Bhagwat and S. O. Shukla

The apparent molar volume of a non-electrolyte in solution does not seem to vary very much with variation in concentration in the range of concentration examined.

The variation of apparent molal volume of a solute with concentration has been investigated by a number of workers (Redlich and Rosenfeld, *Z. physikal. Chem.*, 1931, **155**, 65; Scott and Wilson, *J. Phys. Chem.*, 1934, 38, 951; Prang, *Ann. Phys.*, 1938, 31, 681; Shrinivasan and Prasad, *Trans. Faraday Soc.*, 1939, 35, 1462; Redlich and Bigeleisen, *J. Amer. Chem. Soc.*, 1942, **64**, 758). The change is slight and Redlich and Bigeleisen by measuring density to an accuracy of 0·5 in a million have definitely established that the molal volume of an electrolyte is given by

$$v = V_0 + A\sqrt{C} + BC$$

where A and B are constant and A can be calculated on theoretical basis.

Not much work is done on apparent molal volume of non-electrolytes. Since high accuracy is required in determining density, it was considered advisable to measure the actual volume changes also. The known weight of the substance was added in a microburette and the known volume of water run in by another microburette. The volume change after the solid has dissolved was noted. The concentration of the solution was changed (a) by adding more and more of the solvent to the same solution, and (b) by taking different weights of the solid. Results are as follows. The whole work was carried out at constant room temperature of 20°.

TABLE I

	Acetamide			Urea	
Wt. of substance.	Vol. increase (H_2O).	Wt. of one c.c.	Wt. of substance.	Vol. increase (H_2O).	Wt. of one c.c.
6.7220 g.	6.2 c.c.	1.008	6.1532	4.6	1.33
3.7580	3.4	1.1	4.6490	3.4	1.36
5.5928	5.4	1.03	2.0380	1.5	1.35
4.5900	4.35	1.05	3.9082	2.0	1.34

Dilution of the same solution from 20 c.c. to 50 c.c. did not show any further change in volume which could be detected (up to 0·05 c.c.).

We have for the mean molecular weight M of a solution.

$$M = (1-x)m_1 + xM_x$$

where m_1 is the molecular weight of solvent and M_x, the molecular weight of solute. If d_1 and D are the densities of solvent and solution respectively, then $m_1/d_1 = v_1$, molecular volume of solvent and

$$M/D = \frac{m_1(1-x) + xM_x}{D} .$$

But density D of the solution $= \dfrac{m_1(1-x)+xM_x}{(1-x)v_1+x.v_2}$

where v_2 is the volume of the solute in solution when molar weight is dissolved and that it does not change with dilution.

Hence

$$M/D = (1-x)v_1 + xv_2$$

or

$$\frac{M}{D} \Big/ \frac{m_1}{d_1} = \frac{(1-x)v_1 + xv_2}{v_1} .$$

Since $v_2/v_1 = m$ is constant as v_2 and v_1 are constant

$$\frac{M}{D} \Big/ \frac{m_1}{d_1} = 1 + mx - x.$$

It is thus possible to determine m and hence see whether the volume change caused by dissolving a solid of known weight is constant and does not depend on dilution. The following table illustrates this.

TABLE II

Acetamide in water.					Urea in water.				
$x.$	$M/D.$	$m_1/d_1.$	$\dfrac{M/D}{m_1/d_1}.$	$m.$	$x.$	$M/D.$	$m_1/d_1.$	$\dfrac{M/D}{m_1/d_1}$	$m.$
0.1792	24.15	18.03	1.339	2.89	0.0792	19.67	18.03	1.090	2.13
0.2280	26.03	18.03	1.443	2.94	0.0987	20.23	18.03	1.122	2.23
0.2818	27.90	18.03	1.547	2.94	0.1245	20.87	18.03	1.157	2.24
					0.1501	21.44	18.03	1.189	2.25

Cane sugar in water.					Glucose in water				
0.0216	21.79	18.03	1.208	10.52	0.0154	19.35	18.03	1.073	5.73
0.0257	22.57	18.03	1.251	10.76	0.0235	19.87	18.03	1.102	5.34
0.0377	24.87	18.03	1.379	11.05	0.0320	20.64	18.03	1.144	5.50
					0.0369	21.07	18.03	1.168	5.55
					0.0613	23.21	18.03	1.286	5.66

For a ternary mixture containing X and Y molar fractions of solute whose molecular weights are m_2 and m_3

$$M = (1-X-Y)m_1 + Xm_2 + Ym_3$$

$$d = \frac{(1-X-Y)m_1 + Xm_2 + Ym_3}{(1-X-Y)v_1 + X.v_2 + Y.v_3}$$

where v_1, v_2 and v_3 are the molar volumes in solution for the solvent and dissolved substances. Hence

$$M/d = (1-X-Y)v_1 + X.v_2 + Y.v_3 \qquad \cdots \quad (1)$$

Hence

$$\frac{M/d}{m_1/d_1} = \frac{(1-X-Y)v_1 + X.v_2 + Y.v_3}{v_1}$$

$$= (1-X-Y) + mx + m'.Y$$

where $m = v_2/v_1$ and $m' = v_3/v_1$ which are constant since molar volumes in solution are taken as constants.

TABLE III

Water, (X) Acetamide, (Y) Urea.

	$M/d.$	$(1-X-Y)v_1 + X.v_2 + Y.v_3.$
(i)	$\dfrac{28.18}{1.07} = 26.33$	$0.7539 \times 18 + 0.164 \times 56.96 + 44.16 \times 0.0821 = 26.53$
(ii)	$\dfrac{29.78}{1.095} = 27.19$	$0.7159 \times 18 + 0.1567 \times 56.96 + 44.16 \times 0.1274 = 27.43$
(iii)	$\dfrac{31.87}{1.071} = 29.78$	$0.6636 \times 18 + 0.2627 \times 56.96 + 44.16 \times 0.0737 = 30.16$
(iv)	$\dfrac{30.67}{1.078} = 28.45$	$0.6933 \times 18 + 0.2075 \times 56.96 + 0.0992 \times 44.16 = 28.688.$

The molar volume of acetamide $= 56.96$ and of urea $= 44.16$ as determined before. The application of the formula is interesting, since it proves that even in ternary mixtures the volumes of these dissolved solids in solutions does not change to any marked extent.

CHEMISRTY DEPARTMENT,
HOLKAR COLLEGE, INDORE.

PROF. H K SEN

Born : 1888   Died · June 3, 1945.

OBITUARY

DR. HEMENDRAKUMAR SEN

(1888—1945)

The death of Dr. Hemendrakumar Sen in Calcutta on the 3rd June, 1945, deprived the Society of one of its most distinguished and active Fellows, who served the Society from its very inception in several capacities. With a very few intervals of a year or two, he was all along a member of its Council and became its Secretary, Treasurer, Vice-President and President in turn. Always keen to serve the Society he never failed to respond to its call at any time even at a great inconvenience to him. The Fellows of the Society have lost in him one, who was held in great esteem and sincere affection by them.

The early life of Dr. H. K. Sen was far from a smooth-sailing one and he had to struggle hard against numerous odds and adverse pecuniary circumstances. His father, the late Mr. Prasannakumar Sen was Deputy Inspector of Schools and a member of a cultured middle-class family of East Bengal, belonging to the village of Baldhara in the district of Dacca. Sen was, however, born at Noorpur, Rajbari (Dt. Faridpur), where his father was posted at the time, and he received his early school-education at the Annada H. E. School in Brahmanbaria in the District of Tipperah. He passed the Entrance Examination (equivalent to modern Matriculation) from this school in 1904 in the first division and won a special local scholarship. He then joined the City College, Calcutta, in the first year class and passed the Frst Examination in Arts, now changed into Intermediate Examination, in 1906. He took his B.A. Degree in B. Course from the same College in 1908. It was in this College that Sen first met B. B. Dey (now Dr. B. B. Dey, Director of Public Instruction, Madras) as his class mate, and they readily became fast friends. This friendship between two young souls, initiated in their emotional college days, gradually matured with increasing intimacy in after life into an indissoluble bond of sublime attachment and mutual confidence. Sen's father had a large family and with his small income, reduced further by his retirement, he could not render any help to young Sen to meet the expenses of his education in Calcutta. Sen had, therefore, to depend entirely in those days on his own paltry and precarious earning by means of private tuition, which seldom exceeded thirty rupees a month and often fell below that. With a grim determination and untiring energy Sen fought against all adversities in order to pursue his objective. Many a stout heart would have accepted defeat and made an honourable retreat before such overwhelming obstacles, but Sen was made of a sterner stuff with the characteristic tenacity of an East Bengal youth.

After taking the Bachelor's Degree Sen joined the Presidency College in 1908 for the M.A. Degree Course in Chemistry. The late Sir P. C. Ray was then the Professor of Chemistry there, whose name and fame, and whose patriotism and philanthropy, wielded a great influence upon the student population of Bengal. Many poor students used to receive regular help from Prof. P. C. Ray ; and Sen also first went to him and related his

own story.   The master lost no time in discovering the potentialities that lay hidden in this struggling youth and at once took him in as his private research assistant in the laboratory.   With this help from the Professor, supplemented by his income from private tuition, Sen succeeded in making his two ends meet and carrying himself through the strenuous period of preparation for the M.A. Degree.   It was in this M.A. class of the Presidency College that the present writer came to know Sen and had the good fortune of cultivating a close friendship with him.   Sen took his M.A. Degree in Chemistry in 1911 standing second in Class I with organic chemistry as his special subject, in which he secured exceptionally high and record marks.   While studying for his M.A. Degree Sen used to assist Prof. P. C. Ray in his researches and at the same time to work on problems of his own.   Two pieces of research, completed during this period in collaboration with B. B. Dey, were published in the Zeitschrift fur anorganische Chemie of 1911. These related to the interaction of nitrites with hydrazine salts.   In the early part of 1912, Sen in collaboration with the present writer published another paper in the said journal on the interaction of hydrazine and hydroxylamine with ferricyanides and new methods of estimating hydrazines and ferricyanides.   All these papers were reviewed in the Annual Reports of the Progress of Chemistry for 1911 and 1912.   In 1912 Sen competed for and gained the Premchand Roychand Studentship Prize of the Calcutta University—the most covetable reward at the disposal of the University.   He was appointed Lecturer in Chemistry in the City College, Calcutta, in the same year; but he served only for a few months before leaving for England to join the Imperial College of Science and Technology in London as a research student, where his friend B. B. Dey preceded him some months earlier.   Both the young Indian workers were sympathetically received by the Professors of Chemistry there, who, being impressed by their earnestness and ability, exempted them after the first year from the payments of all laboratory fees and helped them in obtaining substantial research grants from the Chemical Society and other learned bodies.   He worked there for the Doctorate in Science of the University of London, which he obtained in 1915 on the basis of a thesis recording the results of an investigation on the mechanism of reactivity of cyanacetamide in its various condensations.   Sen was probably the first Indian who received the D.Sc. degree of the University of London as its internal student.   Besides the above piece of investigation Sen published at that time a number of other papers dealing with the condensation of ketones and ketonic bodies with phenols and naphthols in the Transactions of the Chemical Society, London. During his stay in London he also participated in the war-work (last World War) of solving many chemical problems in the Imperial College Laboratory, related particularly to the production of important drugs, of which the development of a process for the preparation of β-eucaine was one. Sen succeeded in his task and prepared a few grams of laevo-rotatory β-eucaine for the first time in England.   A gram of this drug was exhibited by Prof. Jocelyn Thorpe at a meeting of the Chemical Society when Sen was congratulated by the President, the late Prof. W. H. Parkin, Jr. of Oxford, and the assembled Fellows on his success.   The process for making β-eucaine was subsequently made over to Boots and Co. for exploitation on a commercial scale.   Sen was offered a research assistantship by Prof. Baker in his laboratory but being eager to return home he left England in 1915.

After his return to India Sen joined the Tata Iron Works at Jamshedpur in 1916 as a chemist in their sulphuric acid plant, but left after a few months for Burma to accept the position of Chief Chemist in the sulphuric acid works of Jamal Brothers there. Later on he went over to the De Souza and Co. as the managing chemist of their chemical works in Burma. During his stay in Burma Sen met his future wife Miss Kalpanarani Sen, the eldest daughter of the late Mr. Nirmalchandra Sen, a very prominent barrister of Rangoon, and the grand daughter of the famous Bengali poet Nabinchandra Sen of Chittagong. The couple was married in 1917 and lived together a very happy life for about three years when it was cut short by the ruthless hand of fate as Sen lost his young wife in 1920 during a child-birth. Struck by this unforeseen calamity in the very prime of his youth Sen, who had a very loving heart, became rather anxious to leave Rangoon and escape from the scenes so painfully reminiscent of his departed wife to whom he was passionately devoted. An opportunity came to him at this psychological moment when he was invited by the late Sir Asutosh Mookerjee to accept the Professorship in Applied Chemistry, then newly created in the University College of Science, Calcutta. Sen accepted this offer and returned immediately to Calcutta. With great zeal and conspicuous ability he served the University in this capacity for over fifteen years durng which he built up the Department of Applied Chemistry from a very small beginning to its present significant position. The present extension of its laboratory and workshop, which he himself planned and designed, and the creation of a separate Board of Higher Studies in Applied Chemistry in the University were entirely due to his unflagging zeal, ardent advocacy and unparalleled devotion.

A succession of devoted workers trained under his tutelage came out of his laboratory, who are now holding their own as capable teachers, research workers and industrial chemists in the country; and his reputation as the foremost industrial chemist in India was established before long. His expert advice on industrial problems was in great demand from various manufacturing firms and he was frequently found even in odd hours of day and sometimes at night too, both at the College and his residence, to be pestered by influential visitors connected with those concerns; for, because of his generous nature and frank disposition, he could not refuse service and interview to anybody even if it involved sacrifice of his own valuable time and energy. The result was that he exposed himself not infrequently to exploitation by others. Possessed with a superabundance of energy he never cared to give rest to his body and mind or to look after his health, which might probably have saved him from the consequence of an early breakdown in after life. He used generally to come to his laboratory early at 8 a.m. in the morning and leave late at about 9 p.m. in the night; his only recreation was occasional drives through the city's street after 10 p.m. in the night or visits to a cinema house. In the beginning he had to lecture to his students on almost all the branches of chemistry, namely, thermodynamics, biochemistry, applied inorganic, organic and physical chemistry, besides chemical engineering. He could not confine himself to any fixed routine or time-table and was in the habit of lecturing for 2-3 hours at a stretch on any particular subject in a day. Being a very good speaker he made his lectures always impressive even without sufficient preparation. In his research programme he did not restrict him·

self to any particular line of study. A variety of problems in both pure and applied chemistry, including bio-chemistry, were tackled in his laboratory by a body of competent research workers. One special problem, that particularly engaged his attention for a pretty long time during this period, was the eradication and utilization of water hyacinth, an exotic evergreen acquatic plant of exuberant growth, which multiplies with extraordinary rapidity and which at one time threatened to block all the smaller water-ways of Bengal. Another problem over which also he devoted a good many years' work was the low temperature carbonisation of coal. Production of power alcohol by fermentation from a particular type of wood (*Excæcaria agallocha*) found in the Sunderbans constituted another long-range problem of research in his laboratory.

In 1922 Sen went out to Europe as Ghosh Travelling Fellow of the University and once again in 1930 in the same capacity to attend the Power Conference at Berlin on invitation. During his stay abroad on the first occasion he worked in the laboratory of Prof. Bone in the Imperial College of Sicence, London, on high pressure reaction technique, and in the Kaiser Wilhelm Institute at Dahlem, Berlin, on certain biochemical problems in collaboration with Prof. Neuberg. He joined the latter in taking a patent on a particular process of fermentation. During his second visit to Europe Sen attended a conference of Austrian chemists at Vienna, where he came into contact with the eminent micro-chemist Prof. Emich of Gratz and his daughter Fraulein Fritzi Emich. The very first acquaintance with the latter drew the two souls together and on Sen's return to India it gradually ripened through regular exchange of ideas by correspondence into intimate friendship and love. The couple were finally married in 1933 at Gratz when Sen went to Europe for the third time in connection with the development of a photographic film industry in India.

In 1936 Sen relinquished his service at the University College of Science to accept the offer of the post of Director at the Lac Research Institute at Ranchi. Here he found a wider sphere of activity and better opportunities for work ; and the Institute under his inspiration and guidance became a centre of research in the field of plastics. With the assistance of a body of earnest workers he introduced many new improvements in the laboratories of the Institute and quite a large number of publications dealing mainly with resins and plastics were issued from these laboratories. Improvements were also effected in the method of production of shellac, and many new ways of its utilization were developed.

Sen received many honours during his life. In 1927 he was elected President of the Chemistry Section of the Indian Science Congress Association held at Lahore. He was the President of the Indian Institute of Chemistry for the terms 1930-32 and once again for 1935-36, an organisation which was practically initiated by him and of which he might rightly be regarded as a foster father. He was one of the Foundation Fellows of the National Institute of Sciences of India. The Indian Chemical Society elected him as their President for 1940-41. He was invited to deliver the Sukhraj Rai Readership lectures in the University of Patna in 1927 and was appointed to deliver the Adhar Chandra Memorial lecture in the University of Calcutta in 1931. The subject of his readership lecture at Patna was " High Temperature Flames and their Thermodynamics," which was sub-

sequently published in the form of a monograph. While still the Director of the Lac Research Institute at Ranchi, he was invited for a second time to deliver the Sukhraj Rai Readership lecture at Patna. He also served as Chairman of many Committees, of which mention may be made of the Fuel Research Committee in 1943 and of Heavy Chemical Industries in 1944 under the Board of Scientific and Industrial Researches of the Government of India. He was a member of the Committee in connection with the Lakshminarayan Memorial Trust for the foundation of the Science and Technological Institute at Nagpur. He represented the Indian Chemical Society in the All-India Board of Chemical Engineering and Technologial Studies, Delhi, for 1944-45. He was also a member of the Committee appointed to report on the establishment of an Imperial Technological Institute at Bombay after the war.

After eight years of active and devoted service at the Lac Research Institute he left it in 1944 to join the Government of Bihar as their Director of Industries, where his service was specially requisitioned to give a shape and effect to their comprehensive scheme of post-war industrial development. Continuous hard-work without rest, recreation and holidays, coupled with all the irregularities of an administrative touring life, already commenced to tell upon his otherwise iron constitution and boundless energy, while he was still at the Lac Research Institute. Domestic troubles and long-standing financial worries contributed in no small measure towards this end. A gradual breakdown of his health surreptitiously set in. But Sen with his usual buoyant spirit and active habits heeded neither the appeals and entreaties of his friends nor even the numerous warnings of the body, and utimately the body had its revenge. In December 1944, soon after his arrival in Calcutta on the occasion of his son's marriage he had a heart stroke from high blood pressure and was forced to take to bed. The illness showed little sign of abatement and slowly undermined his great reserve of vitality till the tragic end came on June 3, 1945 at a rather early age of fifty-six.

By the death of a distinguished scientist and an outstanding applied chemist of Dr. Sen's eminence the country has suffered a severe blow, especially at this critical stage of its history, when his service was sorely needed ; and it might not be possible to fill for many years to come the void left by him. Several chemical and pharmaceutical industries in Bengal have greatly been benefited by his advice and guidance, and it is no wonder that among his numerous admirers and friends will be found quite a respectable body of industrialists and manufacturers.

As a man Sen was loved by all who came in contact with him. ' To know him is to love him ' was truly applicable to his case. In fact, Dr. Sen in his goodness as a man possibly excelled Dr. Sen in his greatness as a scientist. Kind in heart, lovable in disposition, winning in manners, unassuming in nature and habits, warm in conversation, liberal in sympathy and frank in expression he was a sincere friend, ideal teacher, faithful colleague and a generous master. To his friends he would open his heart without any reserve. The present writer can bear eloquent testimony to this from his long personal contact with him. To his colleagues he was always helpful and never allowed any petty jealousy, so common in these days of greed and power, to mar his cordial relations with them. He was a man who would think straight and tell the truth. He possessed the

noble gift in abundance of taking delight in the good fortunes of others. To his pupils he was a never-failing friend and guide, and would do all that lay in his power for their welfare and progress in life. He had about him nothing of the method of an exacting task-master with a rod in hand, but was always gentle and sweet in his directions to his pupils. It was, therefore, quite natural that he gained their universal respect and affection. To all others, his dealings were characterised by a spirit of sympathy and service, which made him feel quite at home in the company of peoples in all walks of life and endowed him with that magnetic power of making friends by first acquaintance.

　　Dr. Sen has left behind him his widow, his only son and his brothers besides a host of relatives, friends, admirers and pupils to mourn his loss with a broken heart. But his manifold virtues will ever remain as a reminder that even in his death he is still alive with us.

　　The writer is indebted to Dr. B. B. Dey for many informations regarding Sen's life, particularly relating to his activities in England as a student, without which the present account would not have been complete.

<div align="right">P. RÂY</div>

LIST OF RESEARCH PAPERS PUBLISHED BY DR. H. K. SEN INDEPENDENTLY AND JOINTLY IN COLLABORATION WITH HIS STUDENTS AND COWORKERS

1. Tetramethylammonium hyponitrite and its decomposition by heat (*J. C. S.*, 1911, 1466).
2. Decomposition of tetramethylammonium nitrite by heat (*Proc. Chem. Soc.*, 1911, p. 4).
3. Detection of nitric acid in presence of an excess of nitrous acid (*Z. anorg. Chem.*, 1912, **74**, 52).
4. Action of hydrazine and hydroxylamine on ferricyanides and a new method for the estimation of hydrazine and ferricyanides (*ibid.*, 1912, **76**, 380).
5. Oxidation of the anhydrides 1:1-dihydroxy-dinaphthyldialkylmethanes (*Proc. Chem. Soc.*, 1913, p. 382).
6. Condensation of camphorquinone with phenols (*ibid.*, p. 155).
7. Condensation of ketones with phenols. Part I. (*J. C. S.*, 1914, 399).
8. Oxidation of α-dinaphthaxanthenes (*J.C.S.*, 1922, 537)
9. Production of hydrogen and oxygen by electrolysis at high pressures (*Inst. Chem. Eng.*, 1932, Jan. 20).
10. Fermentation of α-keto-hexoic acid (*Biochem Z.*, 1923, **143**, 29).
11. Decarboxylation of dimethylpyruvic acid and its preparation (*ibid.*, p. 195).
12. Biochemical transformation of *as*-dichloroacetone into optically active $\delta\gamma$-dichloro-propan-β-ol (*ibid.*, 1924, **151**, 51).
13. Reduction of $\alpha\alpha$-dichloroacetone by yeast (*J. I. C. S.*, 1924, 1, 1).
14. Water hyacinth as a source of fuel (*Trans. II World Power Conference*, 1930, **6**, 221).
15. Cellulose fermentation from horse dung (*J. I. C. S.*, 1934, **11**, 851).
16. Reduction of *sym*-dichloroacetone by yeast (*ibid.*, 1925, 2, 77).

17. Pseudo-methane. Part. I. (*ibid.*, 1925, **3**, 405).

18. Action of *cyclo*hexene oxide in alkali and ammonium halides (*ibid.*, 1927, **4**, 22).

19-24. Formation of heterocyclic compounds. Parts I-VI (*J. C. S.*, 1915, **107**, 1347 ; *J. I. C. S.*, 1927, **4**, 51 ; 1928, **5**, 467 ; 1929, **6**, 309 ; 1930, **7**, 305).

25. Alkylation of hydroxymethylene *cyclo*hexanones (*ibid.*, 1928, **5**, 609).

26. On the ignition temperature of gases (*J.I.C.S.*, 1929, **6**, 44).

27. Studies in the ligno-cellulose group (*ibid.*, p. 673).

28. Uniform propagation of flame (*Nature*, 1931, **127**, 125).

29. Gasification of water hyacinth (*J. I. C. S.*, 1931, **8**, 1).

30. Kinetics of the action of ammonium halides on epichlorohydrin (*ibid.*, 1932, **9**, 509).

31. Explosion of oxy-hydrogen mixtures in soap bubbles (*ibid.*, 1932, **10**, 163).

32. Reaction of diazonium salts with open-chain hydroxymethylene ketones (*ibid.*, 1933, **11**, 347).

33-34. Effect of ultraviolet light on enzymatic reactions (*ibid*, 1935, **13**, 379, 740).

35. Routine gas analysis apparatus (*ibid.*, p. 654).

36. Economics of coal carbonisation (1940, **18**, 73).

37. Some practical problems in low temperature carbonisation of Indian coals (*J. I. C. S. Ind. News Ed.*, 1941, **4**, 37).

38. Resin plastics. (*J.I.C.S.*, 1941, **19**, 47)

39. Manufacture of formaldehyde in India (*J. I. C. S. Ind. News Ed.*, 1942, **5**, 181).

40. Manufacture of thiourea (*ibid*, 1943, **6**, 111).

41. Utilization of Kiri and refuse lac (*ibid.*, 1940, **3**, 29).

42. Estimation of orpiment in shellac (*Bull. Ind. Lac. Res. Inst.*, 1937, No. 26).

43. On the modification of the soft resin in shellac (*Paint Tech.*, 1938, **3**, No. 33, 297).

44. Fluorometric determination of the acid and saponification values of lac (*Proc. Inst. Chem. Ind.*, 1938, 10, Pt. I & II).

45. Injection moulding of shellac plastics (*ibid.*, Pt. I II).

46. Shellac coaltar moulding powder (*Ind. Lac. Res. Inst. Res. Note* No. 20, 1940).

47. Improved method of seedlac manufacture (*Ind. Lac. Res. Inst. Tech. Note* No. 4, 1939).

48. Studies on the constitution of the shellac complex (*ibid.*, Bulletin No. 33, 1939).

49. Modification of shellac and shellac components with melamine and formaldehyde (*ibid.*, *Res. Note* No. 22, 1940).

50. Manufacture of shellac moulding powders (*ibid.*, *Res. Note* No. 25, 1940).

51. Shellac plastics (*ibid.*, *Tech. Note* No. 5, 1940).

52. Lac-melamine and lac-melamine-formaldehyde resins (*Ind. Lac. Res. Inst. Bull.* No. 57, 1944).

METAL-BIGUANIDE POLYHALIDES

By Priyadaranjan Rây and Ajitsankar Bhaduri

A number of polyhalides of copper, nickel, cobalt and chromium biguanide complexes have been prepared and their properties studied. Their general method of preparation consisted in the reaction between a solution of the complex metal halide and that of iodine in KCl, KBr or KI respectively, using either of the solutions in excess. All these polyhalides possess bright colour varying from greenish and bluish black to red and yellowish red, as the quantity of iodine in the molecule diminishes. Some of them form shining, beautiful, bronze-coloured crystals. They are all sparingly soluble in water and their composition and stability vary according to the nature of the central atom. The complex chromium and cobalt *tris*biguanide halides form only pure and saturated polyiodides while those of copper and nickel give unsaturated polyhalides, mostly of the mixed type and derived from mixed halides— the copper complex showing a greater tendency towards this. Some of the compounds have been obtained in two different coloured modifications indicating the occurrence of dimorphism or even of position isomerism. The formation of this peculiar type of compounds between an electronically saturated halogen-ion and a saturated neutral halogen molecule has been discussed in the light of our modern ideas, and their characteristic properties and structure explained.

It is well known that the halogen ions with the exception of F', namely I', Br' and Cl' can in aqueous solution readily associate with the neutral iodine molecule to form the complex polyhalide ions, I'_3, BrI'_2, and ClI'_2 respectively with progressive decrease in strength (*cf.* Jakowkin, *Z. physikal. Chem.*, 1896, **20**, 19 ; Rây and Sarkar, *J. Chem. Soc.*, 1922, **121**, 1449). Even higher polyhalide ions like I'_5 in solution have also been reported by Jakowkin. In the solid state again, only the polyiodides with cations of large volume have been isolated, such as those of ammonium, rubidium and caesium. The last one forms also a solid pentaiodide, CsI_5. Lithium does not give any solid anhydrous tri-iodide. Sodium and potassium tri-iodides have been isolated only in the hydrated states, which break down on dehydration. The relative solubility of these polyiodide compounds runs inversely to their stability. The caesium compound, CsI_3, is known to be difficultly soluble and fairly stable. Tribromides of ammonium, rubidium and caesium have also been obtained in the solid state but no trichloride has yet been known to exist either in the solid state or even in solution. On the other hand, a complete series of solid polyhalides with mixed halogens have been obtained with NH_4^+, K^+, Rb^+ and Cs^+ cations of the composition MXY_2 (Wells and Wheeler, *Z. anorg. Chem.*, 1892, **1**, 442), where M = the cation, $XY_2 = I(Cl$ or $Br)_2$, $BrCl_2$ or $ClBr_2$.

Another interesting class of polyhalides of the composition, $MICl_4$, has been described by Wells and Wheeler (*Z. anorg. Chem.*, 1892, **2**, 259) as also by Weinland and Schlegelmilch (*ibid.*, 1902, **30**, 140). They may be regarded as addition products of ICl_3 to metallic chlorides.

Ephraim has prepared a number of very sparingly soluble, fairly stable polyiodides of some complex metalammines, namely those of nickel, copper, cobalt, zinc and cadmium (*Ber.*, 1921, **54**, 385). The same author has systematically studied the stability of various polyiodide compounds from a measurement of their dissociation pressure at various tem-

peratures in the case of a number of alkali polyhalides (*Ber.*, 1917, 50, 1071) and in the case of the above-mentioned metalammonium compounds from a study of the distribution of iodine between a solvent like carbon disulphide and the residual solid (*loc. cit.*). As a result of his investigation he arrived at the general conclusion that the stability of these polyhalogen compounds increases with the cationic volume, while their solubility continues to decrease. This is obviously related to the reduction of the polarising power of the cation on the highly deformable polyanion as the cationic volume increases. The polyanions are thereby stabilised and do not easily break up by deformation as would have been the case with smaller cations (*cf.* Grace, *J. Chem. Soc.*, 1931, 594 ; Abegg and Hamburger, *Z. anorg. Chem.*, 1906, 50, 403 ; Briggs and Geigle, *J. Phys. Chem.*, 1930, 34. 2250). The polyhalide anions being voluminous in size, when combined with cations of equally large volume, give rise to a close-packing in the crystal lattice stabilising the latter and thus lowering the solubility of the compound ; for, the hydration energy diminishes with increase in the ionic volume and may ultimately fail to overcome the lattice energy.

Rây and Purkayastha (*J. Indian Chem. Soc.*, 1941, 18, 217) have recently described two polyhalogenides of nickel biguanide complex of the following composition ;

$$[Ni(BigH^+)_2]^{Cl}_{I_3} \quad \text{and} \quad [Ni(BigH^+)_2]^{I}_{I_3} ,$$
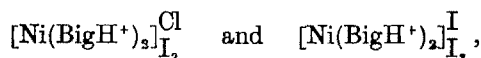
where $BigH$ = one molecule of biguanide, $C_2N_5H_7$.

With a view to testing the validity of Ephraim's conclusion on a wider basis, a series of polyhalogen compounds of both pure and mixed type of complex metalbiguanide cations has been prepared and their properties studied. These compounds may be classified on the basis of their composition as follows :

I. $[X]^{Cl}_{Cl} \cdot [X]^{Cl}_{ClI_2}$ where X = Cu or Ni(BigH$^+$)$_2$

II. $[X]^{Br}_{Br} \cdot [X]^{Br}_{BrI_2}$ where X = „   „

III. $[X]^{I}_{I} \cdot [X]^{Cl}_{ClI_2}$ where X = Cu(BigH$^+$)$_2$

IV. $[X]^{I}_{I} \cdot [X]^{Br}_{BrI_2}$ where X =   „

V. $[X]^{Br}_{I_3}$ where X = Ni(BigH$^+$)$_2$

VI. $[X]^{I}_{I_3}$ where X = Cu or Ni(BigH$^+$)$_2$

VII. $[X]^{Cl}_{I_3}$ where X = Ni(BigH$^+$)$_2$

VIII. $[X](I_3)_3$ where X = Co or Cr(BigH$^+$)$_3$
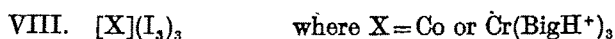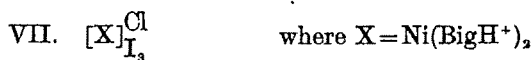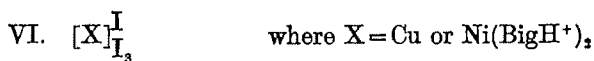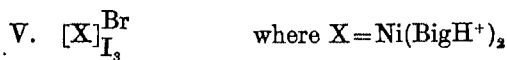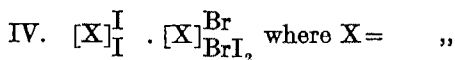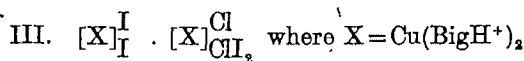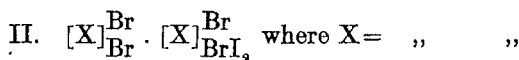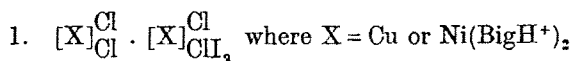
These compounds form sparingly soluble shining crystals of bright colours varying generally from greenish and bluish black to brownish red and red as the quantity of iodine

in the molecule decreases. Some of them are iridescent and show phenomenon of dichroism with metallic lustre. Those containing I'_3 ions are generally less soluble and more stable than those with BrI'_2 and ClI'_2. Of the latter again, those with BrI'_2 are, as might be expected, generally less soluble and more stable than those with ClI'_2. But there are exceptions which we shall presently discuss.

The formation of this peculiar type of compounds between an electronically saturated halogen ion and a neutral halogen molecule like I_2 or Br_2 is usually attributed to the polarisability of both the halogen ions and the halogen molecules. For instance, the mutual induction effect between an iodine ion and an iodine molecule strengthens their respective dipole moments leading to their association into the complex I'_3 ion. The polarisability of the halogen ions and halogen molecules increases with their volume ; hence the order of the stability of the polyhalide anions can be represented as follows :

$$I'_3 > BrI'_2 > Br'_3 > ClI'_2 > ClBr'_2.$$
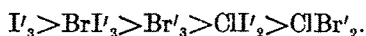
This is in good agreement with their dissociation constant in solution as determined by Dawson (*J. Chem. Soc.*, 1901, 238), Jakowkin (*loc. cit.*) and also by Rây and Sarkar (*loc. cit.*). Chlorine ion, as might be expected from the above considerations, fails to give any stable Cl'_3 ion in solution. Fluorine ion, being very much smaller, is practically non-polarisable, and its polarising power also fails to give rise to the formation of complex ions of the type FI'_2, because of its hydration due to the strong electric field around it.

In the solid state, however, other influences must be taken into consideration, specially the influence of the cations, as already stated. As a rule, cations are practically non-polarisable, but possess a strong polarising power which increases with the charge but diminishes with their size.

An X-ray study of some of the polyhalides of alkali metals by Wyckoff (*J. Amer. Chem. Soc.*, 1920, **42**, 1100) and Mooney (*Z. Krist.*, 1933, **90**, 143 ; 1937, **98**, 324) show that their structure is linear and can be represented as $(I—I—I)'$. The electronic configuration of the ion is given by

$$: \overset{..}{\underset{..}{I}} : \overset{..}{\underset{..}{I}} : \overset{..}{\underset{..}{I}} : ,$$
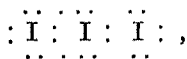
with ten electrons for the central atom, which thereby becomes negative. The structure can, however, be considered as that of a trigonal bipyramid, resembling that of PF_5 and PCl_5 with the halogen atoms at the pyramidal apices and the three unshared electron pairs of the central atom in the equilateral plane (*cf.* Pauling " Nature of the Chemical Bond," 1940, p. 109).

Among the polyhalides of the metal biguanide complexes special reference may be made to the copper biguanide polyhalide which has been obtained in two different modifications—one bluish green and the other brownish red—by the action of copper biguanide iodide on an excess of a solution of iodine in potassium bromide. The bluish green variety first formed, when removed from the solution, changes rapidly into the brownish red modification at the room temperature. As both varieties have the same composition they can only be represented by the following formulae if the possibility of dimorphism be excluded :

(1) $[Cu(BigH^+)_2]_{Br}^{Br} \cdot [Cu(BigH^+)_2]_{I_3}^{I}$ (bluish green)

(2) $[Cu(BigH^+)_2]_{I}^{I} \cdot [Cu(BigH^+)_2]_{BrI_2}^{Br}$ (brownish red)
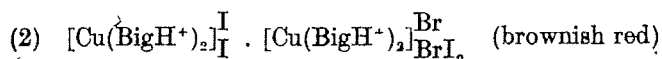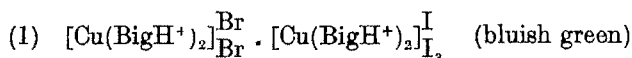
The bluish green variety obviously contains an I'_3 ion, as $[Cu(BigH^+)_2]_{I_3}^{I}$, which has been obtained from $[Cu(BigH^+)_2]I_2$ and KI_3 solution, possesses similar colour. The brownish red variety has also been obtained by a different method (*vide* experimental part). That this contains the BrI'_2 ion is proved by the fact that it has the same colour as that of the compound,

$$[Cu(BigH^+)_2]_{Br}^{Br} \cdot [Cu(BigH^{\cdot})_2]_{BrI_2}^{Br} \cdot$$
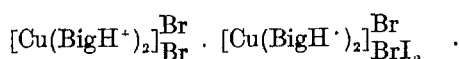
The transformation of the green to the red variety of the aforesaid compound is rather interesting and affords a probable instance of position isomerism. The phenomenon presumably involves the transfer of the iodine molecule from its association with iodine ion to a bromine ion in the other component of the conjugated complex. This, however, seems to suggest that the stability of BrI'_2 ion exceeds that of I'_3 ion contrary to the theoretical considerations as elaborated before and to all previous practical experiences. The geometrical exigency of the lattice structure is evidently responsible for this anomaly, some sort of steric hindrance serving as the operative cause. The possibility of dimorphism also cannot altogether be excluded here.

From a survey of the various metal biguanide polyhalides it will be found that the tervalent cobalt and chromium *tris*biguanide ions give rise to only one type of saturated polyhalide, viz. the pure $[X](I_3)_3$. No mixed or any unsaturated polyhalide was obtained in their case despite all variations in the method of preparation.

With bivalent copper and nickel complexes, all the polyhalides that have been prepared are more or less unsaturated and with the exception of one, $[X]_{I_3}^{I}$, are of the mixed type.

It is difficult to deduce any rigorous quantitative generalisation regarding the stability of these complex metal biguanide polyhalides. The tervalent cobalt and chromium *tris*biguanide polyiodides, which belong to the pure saturated type each containing three I'_3 ions, gradually lose their associated iodine at room temperature in air regenerating the original normal iodides. On the other hand, the bivalent copper or nickel biguanide polyhalides, which are all unsaturated and mostly of the mixed type and may further consist of mixed halides, can be heated to a fairly high temperature like 150-160° without losing the whole of the associated iodine. There is, however, evidence in these cases of the formation of more stable products with lower iodine content. Thus, for instance, the dissociation of the copper biguanide chloro-chloriodide,

$$[Cu(BigH^+)_2]Cl_2 \cdot [Cu(BigH^+)_2]_{ClI_2}^{Cl},$$
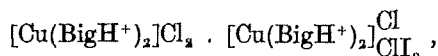
was studied by heating at different temperatures to constant weight under conditions which prevented recondensation of liberated iodine. Plotting the percentage loss of iodine against temperature a curve of the following type was obtained.
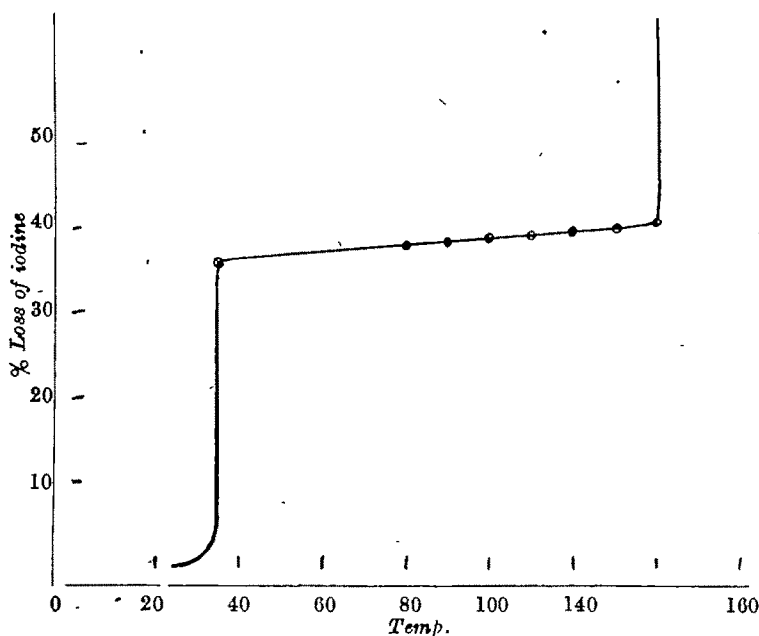
The greater stability of the weaker polyhalide ion (in solution) like ClI'_2 or BrI'_2 in these mixed unsaturated polyhalide crystals compared to that of the more stable (in solution) I'_3 ion of the saturated cobalt or chromium biguanide polyhalide is obviously related to the lattice energy of the crystal based on the geometrical arrangement and radii of the component ions, as already referred to.

It therefore follows that the relative stability of the polyhalide ions in their crystalline compounds will not necessarily follow the same sequence as established by the study of their dissociation constant in solution, where they are practically free from the influence of neighbouring ions. In fact one and the same polyhalide ion may have different stability in its different salts.

Polyhalides of nickel and copper biguanide complexes resemble each other in many respects. Both give unsaturated polyhalides mostly of the mixed type and formed from mixed halides, particularly the copper complex. The chromium and cobalt complexes form only the pure and saturated tri-iodides. All these polyhalides contain variable amounts of water of crystallisation after drying over porous plate. A large variation in this respect for one and the same compound seems to suggest that all the water molecules are not present as water of crystallisation but some at least constitute what is known as lattice and zeolitic water, the amount of which may vary according to circumstances or method of preparation.

EXPERIMENTAL

A. *Copper Biguanide Polyhalides.*

1. *Copper-biguanide Iodo-chloro-chloriodide.*—A cold solution of iodine in potassium iodide was added dropwise to an excess of cold strong solution of copper biguanide chloride

(Rây and Bagchi, *J. Indian Chem. Soc.*, 1939, **16**, 617) with constant stirring. The solution at first became greenish black due likely to the formation of copper biguanide iodo-tri-iodide (*vide infra*), but after a while all on a sudden turned deep red in colour. The resulting red silky crystals were allowed to remain in solution in the cold for half an hour; it was then filtered through a sintered glass funnel, washed several times with ice-cold water and finally dried on a porous plate. The substance was then dried overnight in a desiccator in an atmosphere of iodine vapour. The desiccator was placed inside a refrigerator.

Since these compounds are not very stable due to loss of iodine, the portions for the estimations of different constituents were all weighed out at the same time. {Found : N, 24.44 ; Cl, 6.0 ; I (free), 21.74 ; I (total), 45.05 ; Cu, 11.13. $[Cu(BigH^+)_2]_I^I \cdot [Cu(BigH^+)_2]_{ClI_2}^{Cl}$, $2H_2O$ requires N, 24.43 ; Cl, 6.19 ; I (free), 22.15 ; I (total), 44.35 ; Cu, 11.1 per cent}.

The substance has got a dark red colour and a strong smell of iodine. It is very difficultly soluble in water when dry, but less so when freshly prepared. Iodine is partially removed from the substance by treatment with alcohol. The substance is readily decomposed by dilute acids and slowly loses iodine when kept in air.

When treated with an excess of a solution of iodine in potassium iodide the substance changes to the greenish black complex, iodo-tri-iodide. This shows that the polyhalide ion present in the compound is ClI'_2 and not I'_3.

2. *Copper-biguanide Iodo-bromo-bromiodide.*—As in the case of the previous compound, the substance was prepared from an excess of strong cold solution of copper biguanide bromide (Rây and Bagchi, *loc. cit.*) and a solution of iodine in potassium iodide. {Found : Br, 13.05 ; I (free), 20.92 ; I (total), 42.10 ; Cu, 10.63. $[Cu(BigH^+)_2]_I^I \cdot [Cu(BigH^+)_2] \cdot_{BrI_3}^{Br}$ requires Br, 13.24 ; I (free), 21.25 ; I (total), 42.50 ; Cu, 10.60 per cent}.

The substance forms bright red needle-shaped crsytals with strong smell of iodine and is less soluble than iodo-chloro-chloriodide. Other properties are similar to those of the previous compound. The same compound was obtained also from copper biguanide iodide and an excess of a solution of iodine in potassium bromide (*vide infra*).

3. *Copper-biguanide Iodo-triiodide.*—Dark green, needle-shaped crystals of the compound were obtained from a strong solution of iodine in potassium iodide and that of copper biguanide iodide (Rây and Bagchi, *loc. cit.*) in all proportions. The same compound was obtained also by adding an excess of a solution of iodine in potassium iodide to that of copper biguanide chloride or bromide. {I. Found : I (free), 31.25 ; I (total), 63.05 ; Cu, 7.94. $[Cu(BigH^+)_2]_{I_3}^I$, $2H_2O$ requires I (free), 31.04 ; I (total), 62.80; Cu, 7.86 per cent. II. Found : I (free), 27.50 ; I (total), 54.90 ; Cu, 6.80. $[Cu(BigH^+)_2]_{I_3}^I$, $8.5H_2O$ requires I (free), 27.40 ; I (total), 54.81 ; Cu, 6.87 per cent}.

The second sample was prepared from copper biguanide iodide and an excess of a solution of iodine in potassium iodide. This is the least soluble of the three polyhalides described above.

4. *Copper-biguanide Bromo-bromiodide.*—A concentrated solution of iodine in potassium bromide was added dropwise with constant stirring to a cold solution of copper

biguanide chloride in all proportions. After sometime voluminous bluish black silky crystals appeared, which on stirring changed to yellowish red in colour ; these were allowed to remain in the cold for sometime, and then filtered and washed with ice-cold water containing dissolved iodine. The crystals were afterwards dried as usual. The same compound was obtained when the complex chloride was replaced by bromide. {I. Found :

N, 23.26 ; I (free), 21.24 ; Br, 26.19 ; Cu, 10.58. $[\text{Cu(BigH}^+)_2]^{\text{Br}}_{\text{Br}} \cdot (\text{Cu(BigH}^+)_2]^{\text{Br}}_{\text{BrI}_2}$, $5.5\text{H}_2\text{O}$

requires N, 23.24 ; Br, 26.50 ; I (free), 21.10 ; Cu, 10.56 per cent.. II. Found : Br, 28.09 ; I (free), 21.80 ; Cu, 11.09. Calc. with $2\text{H}_2\text{O}$ requires Br, 28.01 ; I(free), 22.25 ; Cu, 11.15 per cent}.

The second specimen was obtained from an excess of a solution of copper biguanide bromide and a solution of iodine in KBr. When a solution of iodine in KBr was added to an excess of a cold solution of copper biguanide iodide a red product of indefinite composition, containing I, Br' and I_2, was obtained.

5. *Copper-biguanide Bromo-iodo-triiodide.*—When a solution of copper biguanide iodide was added to a solution of an excess of iodine in potassium bromide, silky green needle-shaped crystals separated from the solution. These, when filtered and dried, began changing rapidly to a red coloured product. Hence, a small portion of it was transferred directly from the filtering funnel for the estimation of Cu and associated iodine in the same sample. The green crystals gave Cu : I(free)=1 : 0·94.

The red product formed by its spontaneous transformation in the dry state was found to be identical with the compound 2, copper biguanide iodo-bromo-bromiodide. Hence the green compound possesses the same composition as the latter and is isomeric with it. It should, therefore, be represented by $[\text{Cu(BigH}^+)_2]^{\text{Br}}_{\text{Br}} \cdot [\text{Cu(BigH}^+)_2]^{\text{I}}_{\text{I}_3}$.

6. *Copper-biguanide Chloro-chloriodide.*—When a solution of iodine in potassium chloride was added, drop by drop, to that of copper biguanide chloride in excess in the cold, a greenish black voluminous crystalline precipitate was obtained. This rapidly changed into a yellowish brown granular product. {Found : Cl, 14.18 ; I(free), 25.44 ; Cu, 12.75 ; $[\text{CuBigH}^+)_2]^{\text{Cl}}_{\text{Cl}} \cdot [\text{Cu(BigH}^+)_2]^{\text{Cl}}_{\text{ClI}_2}$, $4\text{H}_2\text{O}$ requires Cl, 14.19 ; I(free), 25.42 ; Cu, 12.78 per cent}.

The same compound was obtained even when an excess of a solution of iodine in potassium chloride was used in the preparation, as also when copper biguanide bromide was treated with an excess of iodine solution in potassium chloride.

The substance possesses an iodoform like odour and is difficultly soluble in water. When kept in a desiccator over H_2SO_4 in an atmosphere of iodine in the cold it lost all its water with slight loss of iodine. The dry product was employed for the study of its dissociation temperatures as plotted in the curve (*vide* theoretical part).

The unstable green voluminous precipitate formed first was quickly transferred from the filtering funnel and the ratio of copper and associated iodine in it was determined. This gave the value 1 : 1, proving its identity with the stable yellowish brown product. Therefore, the colour change is obviously due to the dimorphous nature of the substance.

A solution of iodine in KCl and an excess of cold concentrated solution of copper biguanide bromide or iodide gave granular brown products with no definite composition. A solution of copper biguanide iodide and an excess of iodine in KCl gave a bright green precipitate which remained unchanged in solution in the cold ; but when filtered and dried on a porous plate it changes slowly to a dark red product. Neither of the substances was found on analysis to possess any definite composition. They contained Cl', I' and some I_2.

B. *Nickel Biguanide Polyhalides.*

1. *Nickel-biguanide Chloro-triiodide.*—$[Ni(BigH^+)_2]Cl$ was obtained by the action of a solution of iodine in KI on an excess of nickel biguanide chloride (*cf.* Râ#y and Purakayastha, *loc. cit.*).

2. *Nickel-biguanide Bromo-triiodide.*—A calculated quantity of iodine in KI-solution was added dropwise with stirring to a moderately dilute cold solution of nickel biguanide bromide (Râ#y and Purkayastha, *loc. cit.*). Brownish black silky needle-shaped crystals that separated were left in the cold for half an hour. These were then washed and dried as usual. {Found : Br, 10.56 ; I(free), 33.68 ; I(total), 50.32 ; Ni, 7.70 ; $[Ni(BigH^+)_2]BrI_3$, $2H_2O$ requires Br, 10.54 ; I(free), 33.51 ; I(total), 50.26 ; Ni, 7.75 per cent}.

3. *Nickel-biguanide Iodo-triiodide.*—When a solution of iodine in potassium iodide was added to an excess of nickel biguanide iodide solution green, needle-shaped crystals of iodo-triiodide were obtained. The same compound has also been described by Râ#y and Purkayastha (*loc. cit.*), who obtained it from nickel biguanide chloride and an excess of iodine in KI-solution. The same compound results from nickel biguanide bromide. and an excess of iodine in KI-solution. Nickel biguanide iodide and an excess of iodine in KI-solution gave also a similar product. {Found : I(free), 32.38 ; I(total), 64.66 ; Ni, 7.40 ; $[Ni(BigH^+)_2]_{I_3}^{I}$, H_2O requires I(free), 32.29 ; I(total), 64.58 ; Ni, 7.46 per cent}.

4. *Nickel-biguanide Bromo-bromiodide.*—When a solution of iodine in KBr was treated with a cold concentrated solution of nickel biguanide chloride in any proportion, a greenish black needle-shaped crystalline precipitate was obtained. This was washed and dried as usual. {I. Found : Br, 28.91 ; I(free), 22.74 ; Ni, 10.55.

$[Ni(BigH^+)_2]_{Br}^{Br} \cdot [Ni(BigH^+)_2]_{BrI_2}^{Br}$, $0.5H_2O$ requires Br, 28.97 ; I(free), 22.90 ; Ni, 10.63 per cent}.

The same compound results when an excess of nickel biguanide bromide is substituted for the chloride.

{II. Found : Br, 28.44 ; I (free), 22.50 ; Ni, 10.45 ; Calc. (with 1.5 H_2O) : Br, 28.51 ; I(free), 22.63 ; Ni, 10.45 per cent}.
Nickel biguanide iodide and an excess of a solution of iodine in KBr also gave rise to the same compound differing only in hydration.

{III. Found : Br, 27.52 ; I (free), 21.92 ; Ni, 10.13 ; Calc. (with 3.5H_2O) : Br, 27.63 ; I(free), 21.93 ; Ni, 10.13 per cent}.

From a solution of iodine in KBr and a solution of nickel biguanide iodide in excess a product of variable composition was obtained, which on drying on the porous plate formed beautifully shining bronze-coloured silky crystals.

5. *Nickel-biguanide Chloro-chloriodide.*—Greenish yellow silky needle-shaped crystals with a bronze tinge were obtained from a cold solution of nickel biguanide chloride and a concentrated solution of iodine in KCl, using either in excess. The crystals were allowed to settle and filtered through a sintered glass funnel, washed and dried as usual. Samples, however, differed in water of hydration. {I. Found : Cl, 13.66 ; I (free), 24.39 ; Ni, 11.41. $[Ni(BigH^+)_2]_{Cl}^{Cl}$. $[Ni(BigH^+)_2]_{CII_3}^{Cl}$, $6H_2O$ requires Cl, 13.71 ; I(free), 24.70 ; Ni, 11.44 per cent. II. Found : Cl, 13.10 ; I(free), 23.75 ; Ni, 10.96 ; Calc. (with $8.5H_2O$) : Cl, 13.26 ; I(free), 23.73 ; Ni, 10.96 ; per cent}.

From a solution of iodine in KCl and that of nickel biguanide bromide, using an excess of either, a yellowish green silky needle-shaped crystalline precipitate was obtained. When filtered and washed it changed readily to a bronze-coloured product. But it gave no definite composition despite the ratio of Ni : I (associated) remaining 1 : 1.

The yellowish green crystalline precipitate obtained from an excess of a solution of nickel biguanide iodide and a solution of iodine in KCl was found to be of indefinite composition with the ratio of Ni : I (associated), however, remaining 1 : 1. A bronze-coloured product of similar indefinite composition was obtained using the iodine solution (in KCl) in excess.

C. Cobalt tris*Biguanide Triiodide.*

A solution of iodine in KI was added dropwise to that of an excess of cobalt *tris*-biguanide chloride (Rây and Dutt, *J. Indian Chem. Soc.*, 1939, **16**, 621) in the cold. The yellow precipitate of cobalt *tris*biguanide iodide appeared first, which rapidly turned into a deep black pasty mass and adhered to the sides of the beaker and to the stirring rod. It was left in the cold for half an hour when it became granular. This was then filtered, washed and dried as usual. The use of an excess of iodine solution in KI gave the identical product. {Found : I(free), 43.15, 43.88 ; I(total), 65.36, 65.80 ; Co, 3.39, 3.40. $[Co(BigH^+)_3](I_3)_3$, $13H_2O$ requires I(free), 43.81 ; I(total), 65.72 ; Co, 3.39 per cent}.

The same product was obtained when cobalt *tris*biguanide bromide or iodide was substituted for the chloride.

The substance forms shining black needle-shaped crystals with strong smell of iodine. It is somewhat soluble in water and alcohol. The substance is rather unstable ; it loses all its associated iodine slowly when kept exposed to air and changes ultimately to the yellow cobalt *tris*biguanide iodide.

A solution of iodine in KBr or in KCl, on the other hand, precipitates only the corresponding cobalt *tris*biguanide bromide or chloride under all circumstances.

D. Chromium tris*Biguanide Triiodide.*

A cold solution of iodine in potassium iodide was added, drop by drop, with stirring to a cold concentrated solution of chromium *tris*biguanide chloride (Rây and Saha, *J. Indian Chem. Soc.*, 1937, **14**, 670) in excess. The orange-red chromium *tris*biguanide iodide, which appeared first, quickly changed into a black coloured product. This formed, as

in the case of cobalt, a pasty mass which adhered to the sides of the beaker and to the stirring rod. But it slowly became crystalline when it was allowed to stand in the cold for half an hour. This was washed and dried as in the previous case. {Found : I(free), 47.75 ; I(total), 71.74 ; Cr, 3.26. [Cr(BigH·)$_3$](I$_3$)$_3$, 5.5H$_2$O requires I (free), 47.71 ; I(total), 71.58 ; Cr, 3.26 per cent}.

The same compound was obtained also by using an excess of a solution of iodine in KI, which, however, differed in the water of hydration. {Found : I(free), 46.26 ; I(total), 69.29 ; Cr, 3.13. Calc. (with 8.5H$_2$O) : I(free), 46.15 ; I(total), 69.23 ; Cr, 3.15 per cent}.

It resembles the corresponding cobalt *tris*biguanide polyiodide in all respects. Identical products were obtained when chromium *tris*biguanide bromide or iodide was substituted for the chloride. With a solution of iodine in KBr or KCl, on the other hand, only the chromium *tris*biguanide bromide or chloride separated from the solution under all circumstances as in the case of cobalt.

CONDENSATION OF PHENOLS AND PHENOLIC ETHERS WITH ACETONE DICARBOXYLC ACID. USE OF CONDENSING AGENTS OTHER THAN SULPHURIC ACID. A NEW NON-ACIDIC CONDENSATION PRODUCT

BY V. M. DIXIT, A. M. KANKUDTI AND L. M. MULAY

Resorcin has been condensed with acetone dicarboxylic acid in the presence of (*i*) anhydrous aluminium chloride, (*ii*) phosphorous oxychloride, (*iii*) phosphorous pentoxide and (*iv*) thionyl chloride, as condensing agents. In each case a new non-acidic condensation product has been obtained in addition to the expected 7-hydroxycoumarin-4-acetic acid. A formula of the dilactone of $\beta\beta$-di-(2 : 4-dihydroxyphenyl) glutaric acid has been provisionally suggested for the new compound.

Phenols, naphthols and their ethers have been condensed with β-diketonic esters in the presence of several condensing agents *e.g.* sulphuric acid (Pechmann and Burton, *Annalen*, 1894, **261**, 167), phosphorous oxychloride (Naik, Desai and Trivedi, *J. Indian Chem. Soc.*, 1929, **6**, 801), anhydrous aluminium chloride (Shah and Sethna, *J. Chem. Soc.*, 1938, 228); alcoholic hydrochloric acid (Appel, *ibid.*, 1935, 1031); phosphorus pentoxide (Chakravarti, *J. Indian Chem. Soc.*, 1931, **8**, 129); sodium ethoxide (Chakravarti, *loc. cit.*); the main products in almost all cases being coumarins.

Phenols, and their ethers have also been condensed with a β-diketonic acid, acetone dicarboxylic acid. In most of the reactions the condensing agent has been sulphuric acid and the following types of compounds have been obtained :—(1) Coumarin-4-acetic acids (Dey, *J. Chem. Soc.*, 1915, **107**, 1606 ; Limaye, *J. Indian Chem. Soc.*, 1927, **4**, 158) ; (2) β-aryl glutaconic acids (Limaye and Bhave, *ibid.*, 1931, **8**, 137 ; Dixit, *ibid.*, 1931, **8**, 787 ; Gogte, *Proc. Indian Acad. Sci.*, 1934, **1**, 48) ; (3) $\beta\beta$-diaryl glutaric acids : *ortho* condensation (Dixit and Gokhale, *J. Univ. Bombay*, 1934, **3**, 95), *para* condensation (Gogte, *Proc. Indian Acad. Sci.*, 1937, **5A**, 535) ; (4) $\beta\beta$-diaryl butyric acids (Bokil and Vyas, *Rasayanam*, 1939, 198) ; (5) hydrindenylidene acetic acids (Limaye and Gogte, *J. Univ. Bombay*, 1935, **4**, 135).

Phosphorus pentoxide has been used by Chakravarti (*loc. cit.*) to condense resorcin with acetone dicarboxylic acid and he obtained 7-hydroxycoumarin-4-acetic acid as the product.

Anhydrous alumininium chloride has been used by Bhave (*Rasayanam*, 1939, 180) to condense acetone dicarboxylic acid with resorcin dimethyl ether, the condensation product being $\beta\beta$-(2 : 4-dimethoxyphenylene)-1 : 5-*bis*-glutaconic acid.

The present work was undertaken with a view to studying the condensation of phenols and phenolic ethers with acetone dicarboxylic acid in the presence of condensing reagents other than sulphuric acid.

Resorcin has been condensed with acetone dicarboxylic acid (1 : 1 mol.) in the presence of (*i*) aluminium chloride, (*ii*) phosphorus oxychloride, (*iii*) phosphorus pentoxide and (*iv*) thionyl chloride. In the case of (*i*) and (*iv*) carbon disulphide and benzene have been used as solvents respectively while in the remaining two no solvent is used.

In each of these reactions, the crude condensation product could be separated into two parts—(A) an acid, and (B) a non-acid.

The acid (A) on crystallisation from alcohol separates as shining long needles and is identified with 7-hydroxycoumarin-4-acetic acid by mixed m.p. and conversion into 4-methylumbelliferone. The non-acid (B) crystallises from alcohol in very small prisms blackening at 210° and melting at 290°. An alcoholic solution of the substance gives a greenish black colouration with ferric chloride indicating the presence of free OH groups. It forms neither a phenylhydrazone nor a semicarbazone.

An ebullioscopic determination shows that its molecular weight is in the neighbhourhood of 310, thus indicating a condensation between two molecules of resorcin and one of acetone dicarboxylic acid.

An estimation of the OH groups by the acetylation method showed the presence of two free OH groups in the substance.

To arrive at the constitution of this non-acidic substance, it has been subjected to the following reactions :

(1) *Alkaline hydrolysis.*—The substance is hydrolysed by both alcoholic and aqueous sodium hydroxide (5%). In either case, the products of hydrolysis are (*i*) 7-hydroxycoumarin -4-acetic acid and (*ii*) resorcin, which is isolated by converting it into its 4 : 6-dibromo derivative.

(2) *Acidic hydrolysis.*—A solution of the substance in sulphuric acid (75%) is refluxed for a couple of hours. This gives almost quantitative yields of (*i*) 7-hydroxycoumarin-4-acetic acid and (*ii*) resorcin.

(3) *Hydrolysis and methylation* is carried out according to Robertson and Canter (*J. Chem. Soc.*, 1931, 1875). This gives two products : (*i*) β-2 : 4-dimethoxyphenylglutaconic acid and (*ii*) resorcin dimethyl ether.

(4) *Oxidation.*—The substance is oxidised by (*i*) chromic acid, (*ii*) alkaline potassium permanganate and (*iii*) hydrogen peroxide (10 vols.) but in none of these reactions could a workable product be separated and in each case nearly 50% of the original substance were recovered unchanged.

(5) *Methylation.*—The substance could not be methylated.

(6) *Acetylation* gives diacetyl derivative (m.p. 186°). An attempt to deacetylate it by heating with sodium hydroxide produces 7-hydroxycoumarin-4-acetic acid and resorcin.

(7) *Benzoylation* gives a dibenzoyl derivative (m.p. 206°) which on hydrolysis with alkali decomposes to 7-hydroxycoumarin-4-acetic acid and resorcin.

(8) *Heating at m.p.*—No marked change is effected by heating.

In view of the foregoing results, the formula of dilactone of ββ-di-(2 : 4-dihydroxyphenyl)-glutaric acid (II, R′ = OH ; R″ = H) has been provisionally assigned to the non-acidic condensation product (B).

The reaction between resorcin and acetone dicarboxylic acid can be shown to take place in the following three ways to produce this compound :—

(i)

[structure (I)]

(I)

(Unstable)

[structure (II)]

(II)
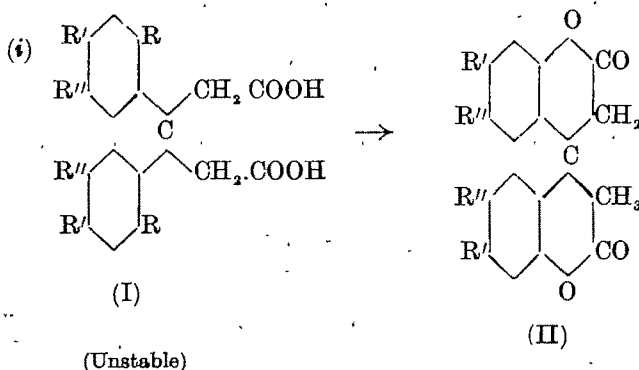
[ββ-di-(2 : 4-dihydroxyphenyl)-glutaric acid] (I, R=R'=OH ; R''=H)

Acetone dicarboxylic acid is known to condense in its ketonic form with phenols to give ββ-diaryl glutaric acids (cf. Dixit and Gokhale, loc. cit.).

(ii)

[structure] → (I, R=R'=OH ; R''=H) → (II, R'=OH ; R''=H)
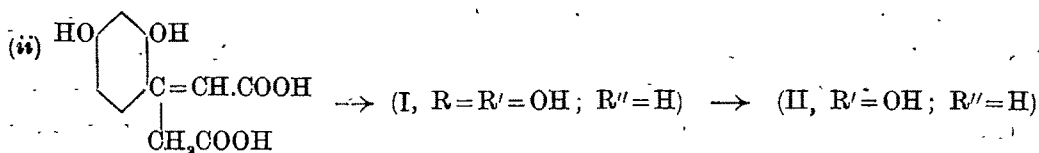
A similar additive reaction between a molecule of p-cresol ethyl ether and a molecule of β-(2-ethoxy-5-methylphenyl)-glutaconic acid has been reported by Gogte (Proc. Indian Acad. Sci., 1935, 2, 196), the product being ββ-di-(2-ethoxy-5-methylphenyl)-glutaric acid (I, R=OEt ; R'=H ; R''=Me). This compound changed to (i) the dilactone (II, R'=H ; R''=Me) under the influence of sulphuric acid (80%) and (ii) to 6-methylcoumarin -4-acetic acid (III) on hydrolysis with alkali.

(I, R=OEt ; R'=H ; R''=Me)   Hydrolysis (alkali) ───────→   [structure (III)]

              ↓ 80% H₂SO₄

(II, R'=H ; R''=Me)   (III)

(iii)

[structure (IV)]   Resorcin (1 mol) ─────→   [structure (V)]   → (II, R'=OH ; R''=H)

(IV)

(V)
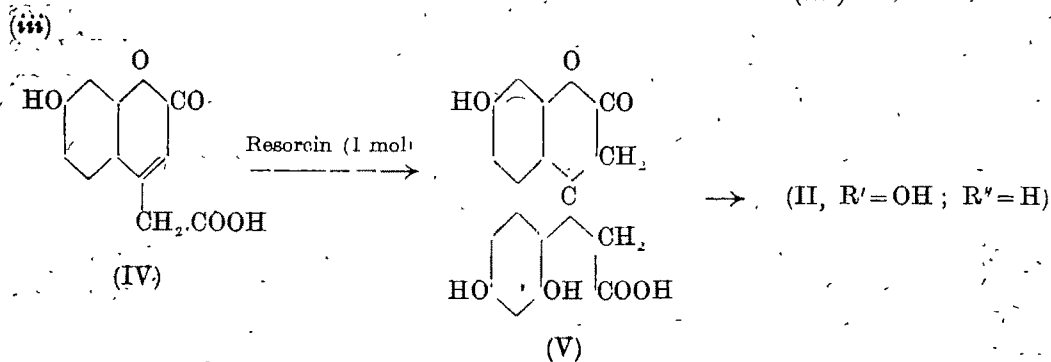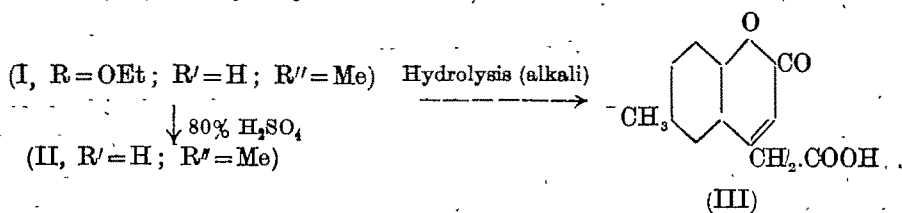
An intermediate monobasic lactonic acid of the type (V) has been mentioned by Gogte (*loc. cit.*) during the conversion of his $\beta\beta$-di-(2-ethoxy-5-methyl phenyl)-glutaconic acid (I, R = OEt ; R′ = H ; R″ = Me) into the corresponding dilactone (II, R′ = H ; R″ = Me).

A direct synthesis of the dilactone has, therefore, been attempted by the condensation of resorcin dimethyl ether with β-(2 : 4-dimethoxyphenyl)-glutaconic acid (1 : 1 mol.) in the presence of sulphuric acid (80%) according to Gogte's method and the subsequent demethylation of the product. This is not, however, successful. The reaction has been tried under different conditions and in the presence of different condensing agents but without success.

The direct synthesis is then attempted by condensing resorcin with 7-hydroxycoumarin -4-acetic acid (1 : 1 mol) in the presence of (1) sulphuric acid (75% and 100%), (2) phosphorus oxychloride, (3) phosphorus pentoxide, (4) aluminium chloride and (5) thionyl chloride as condensing agents. A small quantity of the dilactone has been obtained only in the reaction with phosphorus oxychloride. In all other cases, the 7-hydroxy-coumarin-4-acetic acid is recovered unchanged. It seems, therefore, that in the formation of the dilactone the reaction between acetone dicarboxylic acid and resorcin takes the course as shown in (*i*) and that the acetone dicarboxylic acid acts in the ketonic form. According to the literature available, the most satisfactory conditions for this type of reaction are to carry out the condensation at low temperature and under the influence of sulphuric acid (75%, Dixit and Gokhale, *loc. cit.*) and when resorcin is condensed with acetone dicarboxylic acid under these conditions, the dilactone is obtained in fairly good quantity as compared with the 7-hydroxycoumarin-4-acetic acid. This lends support to the course of the reaction represented in (*i*).

Further investigation of the non-acidic condensation product is being continued with a view to confirming its constitution and to studying some of its expected synthetical reactions. Work is also in progress for studying the use of new condensing agents like sulphuryl chloride, anhydrous zinc chloride, sodium ethoxide etc. for the condensation of phenols, naphthols and their ethers with acetone dicarboxylic acid.

EXPERIMENTAL

Acetone dicarboxylic Acid.—Anhydrous citric acid (50 g.) was heated with concentrated sulphuric acid (90 c.c.) at 60-65° till the effervescence of carbon monoxide subsided. The mixture was then cooled and poured over crushed ice (about 160 g.) with stirring and kept in a cool place for 1 hour. A crystalline precipitate soon separated. It was filtered on flannel, washed with small quantities of ethyl acetate, dried on a porous plate and crystallised from ethyl acetate. It has to be preserved under vacuum in a desiccator, yield 75%, white needles, m.p. 136° (decomp.).

Condensation of Resorcin with Acetone Dicarboxylic Acid.

(a) In the presence of Anhydrous Aluminium Chloride.—Anhydrous aluminium chloride (27 g.) was added in small quantities to a fine suspension of acetone dicarboxylic acid (15 g.) and resorcin (11 g.) in dry carbon bisulphide (150 c.c.) and the mixture was re-fluxed on a water-bath for about 4 hours with a condenser fitted with a calcium chloride guard tube. The carbon bisulphide was distilled off and the dry orange-coloured residue

was mixed with crushed ice (about 200 g.) containing a small quantity of hydrochloric acid. The white solid was filtered off, washed with water and then shaken with a solution of sodium bicarbonate (about 10%). A part of it dissolved and the solution was separated from the residue by filtration.

The filtrate on acidification gave 7-hydroxycoumarin-4-acetic acid, in long shining white needles from dilute alcohol, m.p. 203-204° (decomp.), yield 5.4 g.. Its alkaline solution shows a beautiful blue fluorescence (mixed m.p. with an authentic specimen). It was decarboxylated to 4-methylumbelliferone, m.p. 182°. (Found : C, 59.62 ; H, 3.90 per cent. Equiv., 219. Calc. for $C_{11}H_8O_5$: C, 59.72 ; H, 4.07 per cent. Equiv., 220).

The non-acidic residue was washed with water and crystallised from dilute alcohol in prismatic crystals which blacken at 210° and melt at 290°, yield 6 g. It is soluble in alcohol, acetone, ethyl acetate, methyl alcohol ; sparingly soluble in water, benzene, petroleum ether and carbon tetrachloride. It gives a greenish colouration in alcoholic solution with ferric chloride. (Found : C, 64.96 ; H, 4.20. $C_{17}H_{12}O_6$ requires C, 65 37 ; H, 3.84 per cent).

(b) *In the presence of Phosphorus Oxychloride.*—Phosphorus oxychloride (11 g.) was gradually added to a mixture of acetone dicarboxylic acid (5 g.) and resorcin (3.8 g.) in a flask fitted with an air condenser with a calcium chloride guard tube with constant shaking and cooling. It was then allowed to stand overnight and then poured over crushed ice (about 50 g.). The yellowish solid, which separated, was filtered, washed and treated with sodium bicarbonate solution as given under (a) to separate the acid 7-hydroxy-coumarin -4-acetic acid (2.8 g.) and the dilactone (3.2 g.). Both of these were found identical with the corresponding substances obtained in (a).

(c) *In the presence of Phosphorus Pentoxide.*—To an intimate mixture of acetone dicarboxylic acid (15 g.) and resorcin (11 g.) phosphorus pentoxide (15 g.) was added in small quantities. The mixture soon melted to a viscous liquid and a vigorous reaction followed with liberation of heat. After the reaction subsided, the flask was fitted with a calcium chloride guard tube and heated on a water-bath at 75-80° for about 3 hours. The reaction mixture was mixed with crushed ice (about 50 g.). A semi-solid mass separated which on standing overnight changed to a powder from which 7-hydroxycoumarin- -4-acetic acid (5 g.) and the dilactone (13 g) were isolated by treatment with sodium bicarbonate according to the process given under (a).

(d) *In the presence of Thionyl Chloride.*—A mixture of thionyl chloride (5.5 c.c.) and dry benzene (10 c.c.) was gradually added to a solution of acetone dicarboxylic acid (15 g.) and resorcin (11 g.) in dry benzene (40 c.c.) in a flask through the condenser tube. The mixture became slightly warm due to the heat of the reaction and developed a blue-black colour. After keeping the reaction mixture for 24 hours the benzene layer was decanted off and the pinkish solid was mixed with crushed ice (about 50 g.). The white powder, which separated, was filtered, washed and separated by sodium carbonate into 7-hydroxy-coumarin-4-acetic acid (3 g.) and the dilactone (7 g.) as mentioned under (a).

Hydrolysis of the Dilactone.

(a) *By Aqueous Alkali.*—The dilactone (2 g.) was refluxed with sodium hydroxide (50 c.c. of 5%) for 2 hours. The mixture was cooled and acidified and the solid separating was filtered, washed and treated with sodium bicarbonate solution which dissolved most of it. This was filtered and the filtrate was then acidified. The acidic substance, which separated, was crystallised from dilute alcohol as needles (1 g.), m.p. 203° (decomp.). It was identified as 7-hydroxycoumarin-4-acetic acid.

The filtrate after removing the solid product of hydrolysis was acidified and a brominating mixture containing potassium bromide and potassium bromate (100 c.c. of 0.4 N) was added to it in small quantities with good shaking after each addition. A reddish flocculent precipitate appeared in a short time. It was filtered, washed with water and crystallised from dilute alcohol as white silky needles, m.p. 110° (decomp.), yield 0.8 g. It was identified with a known specimen of 4 : 6- resorcin dibromide by mixed m.p. (Found : Br, 59.53. Calc. for $C_6H_4O_2Br_2$: Br, 59.68 per cent).

It was observed that bromination with a stronger brominating mixture (1 N)produced 2 : 4-dibromoresorcin as short needles, m.p. 92° instead of the 4 : 6-dibromo compound.

(b) *By Alcoholic Sodium Hydroxide* (5%).—The dilactone (2 g.) was hydrolysed with alcoholic sodium hydroxide (5%) according to the method described above. On removal of alcohol and acidification a white precipitate was obtained. This was identified as 7-hydroxycoumarin -4-acetic acid. The filtrate on bromination gave 4 : 6 dibromoresorcin.

(c) *By Acid.*—The dilactone (2 g.) was refluxed with sulphuric acid (50 c.c. of 75%) for about 2 hours. The mixture was cooled and poured on ice. The separated white powder was removed by filtration, washed and treated with sodium bicarbonate solution in which it dissolved and was precipitated by acid. White shining needles from dilute alcohol, m.p. 202° (decomp.). It was identified as 7-hydroxycoumarin-4-acetic acid by mixed m.p. and conversion into 4-methylumbelliferone. The filtrate on bromination gave 4 : 6-dibromoresorcin, m.p. 110°.

Hydrolysis and Methylation of the Dilactone—A mixture of the dilactone (10 g.), methyl alcohol (80 c.c.) and sodium hydroxide solution (80 c.c. of 20%) was heated under reflux for a short time and cooled. Dimethyl sulphate (40 g.) was added gradually with occasional cooling. The mixture was then refluxed for 2 hours, and the reaction was completed by adding sodium hydroxide (30 c.c. of 20%) and heating it for about 30 minutes. On cooling, an oily layer separated. This was extracted by ether and the aqueous portion on acidification gave a white powder. This was filtered, washed and purified through its copper salt, yellowish white prismatic plates from alcohol, m.p. 169° (decomp.), yield 4 g.

This acid was identified with β-2 : 4-dimethoxyphenylglutaconic acid (m.p. 169-170°, decomp.) which was prepared by condensing resorcin dimethyl ether with acetone dicarboxylic acid in the presence of phosphorous oxychloride as the condensing agent, according to Bawadekar (M.Sc. Thesis to the Bombay Univ., 1941). The identity of the acid was further confirmed by preparing its semi-anilide (m.p. 165°) and methyl

ester (m.p. 112°). (Found : C, 58.5 ; H, 5.16. Equiv. 132.05. Calc. for $C_{13}H_{14}O_6$: C, 58.64 ; H, 5.26 per cent. Equiv., 133.)

The dark liquid obtained from the ethereal extract was purified by distillation and was found identical with resorcin dimethyl ether, almost colourless liquid, b.p. 217°, yield 3.5 g. It was brominated by bromine in acetic acid and the product was crystallised from dilute alcohol as long pinkish needles, m.p. 139°. The dibromo derivative of resorcin dimethyl ether mentioned in literature has a m.p. 137-138°.

Attempted Methylation of the Dilactone.—The dilactone (2 g.) was dissolved in pyridine (10 c.c.) and the mixture was refluxed with dimethyl sulphate (6 g.) for 2 hours. After evaporation of the pyridine, the mixture was poured into ice-water, from which the original dilactone was recovered unchanged.

Acetylation of the Dilactone.—The acetyl derivative of the dilactone was prepared as usual using acetic anhydride and a few drops of concentrated sulphuric acid. It was crystallised from glacial acetic acid as flat white prisms, m.p. 186°. (Found : C, 63.52 ; H, 4.18. $C_{21}H_{16}O_8$ requires C, 63.63 ; H, 4.04 per cent).

Benzoylation of the Dilactone.—The dilactone was benzoylated in pyridine solution with benzoyl chloride. It was crystallised from acetone as prismatic plates, m.p. 206°. (Found : C, 71.23 ; H, 3.74. $C_{13}H_{20}O_8$ requires C, 71.50 ; H, 3.84 per cent).

When benzoylation was carried out in the presence of dilute sodium hydroxide another substance with a higher m.p. (260°) was obtained. This is suspected to be the *O*-benzoyl derivative. Its exact nature, however, is still under investigation.

Heating at m.p..—On heating the dilactone at its m.p. in a paraffin-bath for about 1 hour, a partially charred mass and a small quantity of white sublimate were obtained. The sublimate showed tests of resorcin and the charred mass on purification with animal charcoal yielded about 70% of the original substance.

Synthesis of the Dilactone from 7-Hydroxycoumarin-4-acetic Acid.—Phosphorus oxychloride (10 g.) was slowly added to a mixture of 7-hydroxycoumarin-4-acetic acid (5 g.) and resorcin (3.5 g.) which was then kept for about 48 hours with shaking at intervals. It was then poured into ice (about 25 g.). The solid separating was treated with sodium bicarbonate solution. Most of it dissolved leaving only a small quantity of non-acidic residue (0.5 g.). This was crystallised from alcohol in microscopic prismatic crystals, m.p. 290° (with charring at 210°). Its alcoholic solution turns greenish with ferric chloride. Its melting point was not depressed on mixing it with an equal quantity of the non-acidic substance obtained by condensing acetone dicarboxylic acid with resorcin described above.

Other condensing agents like phosphorous pentoxide, thionyl chloride, sulphuric acid (75%), and dry hydrochloric acid gas were tried with a view to improving the yield, but without success. Condensation of resorcin with the ethyl ester of 7-hydroxycoumarin-4-acetic acid was tried in the presence of sodium ethoxide, but there was hardly any reaction.

SYNTHESIS OF THE DIETHYL ESTER OF AN ISOMER OF THE DICARBOXYLIC ACID ($C_{12}H_{20}O_4$)—A DEGRADATION PRODUCT OF β-VETIVONE*

By BIDYUT KAMAL BHATTACHARYYA

Michael condensation between ethyl *cyclo*pentanone·carboxylate and ethyl α-crotonate followed by hydrolysis and esterification furnishes ethyl *cyclo*pentan-1-one-2-(ethyl β-n-butyrate)-2-carboxylate which, on Reformatsky's reaction, followed by unsaturation and hydrogenation, yields ethyl *cyclo*pentane 1-(ethyl- α-propionate)-2- β-n-butyrate.

Pfau and Plattner (*Helv. Chim. Acta*, 1940, **23**, 768) have obtained the dicarboxylic acid (I) through a series of elegant degradative reactions on β-vetivone which occurs in the oil of vetiver.
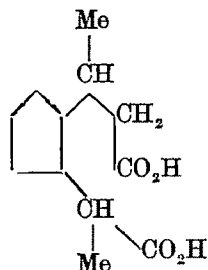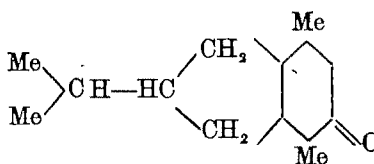
(I)   (II)

In order to furnish direct synthetical confirmation of the azuline skeleton, Cook and Coats (*J. Chem. Soc.*, 1942, 559) have claimed the synthesis of the apo-ketone (II). At the same time we have undertaken the synthesis of the dibasic acid (I), which possesses a comparatively simple structure, along the following line.

Michael condensation between ethyl α-crotonate and ethyl *cyclo*pentan-1-one-2-carboxylate has been carried out in presence of different molecular proportions of potassium ethoxide. The optimum yield of (III, R=CO₂Et ; R₁=Et) is obtained when an alcoholic solution of the unsaturated ester is slowly added to the mixture of the β-ketonic ester and 0.14 mole of potassium ethoxide in alcoholic solution, well cooled in freezing mixture, and the reaction is allowed to proceed for seven days. Due to the possibility of ring fission, which may occur during the above condensation, the use of a comparatively large quantity of alkoxide has been always avoided. Eventually the fission does actually take place to yield (IV) whenever the temperature of the reaction is not kept sufficiently low. Further, time has been found to have considerable influence on the yield of the final product. The condensation product (III, R=CO₂Et ; R₁=Et) is hydrolysed with hydrochloric acid to give (III, R=R₁=H) which is rather hygroscopic. The same keto-acid is also obtained from (IV) by means of Dieckmann condensation followed by hydrolysis with 20% sulphuric acid. The ester of the above acid is condensed with ethyl cyanoacetate according to the method of Cope (*J. Amer. Chem. Soc.*, 1937, **59**, 2327) when a poor yield of (V, R=Et ; R₁=CN) is obtained. The methylation of the above unsaturated ester has been carried out following Cope and Hancock (*ibid.*, 1938, **60**, 2903). The disappointing yield in the Knoevenagel reaction has, however, prevented us from proceeding any further along this line.

·The keto-ester (III, R=H ; R$_1$=Et) is refluxed with ethyl 2-bromopropionate and zinc in benzene solution. The resulting lactone (VI) is insoluble in ice-cold 10% caustic soda solution and is resistant to the usual reducing agents, *e.g.*, red phosphorus and iodine ; zinc amalgam and concentrated hydrochloric acid (Copp and Simonsen, *J. Chem. Soc.*, 1940, 416) and zinc dust and caustic alkali. The lactonic ring has been opened up with phosphorus pentabromide and then treated with alcohol. The bromo-ester, thus obtained, can neither be made to split off a molecule of hydrobromic acid with quinoline or pyridine nor could it be reduced with zinc dust and acetic acid (*cf.* Linstead and Meade, *ibid.*, 1934, 935) ; but it can easily be converted into the unsaturated acid (V, R=H; R$_1$=Me) when refluxed with methyl alcoholic caustic potash solution. The diethyl ester of the above acid is hydrogenated over Adam's catalyst and on hydrolysis with alkali furnishes a gummy acid (I) which solidifies after standing for several months. It has been crystallised from dilute methanol, m.p. 129-31° ; while the inactive acid obtained by the degradative reaction on β-vetivone metls at 168-69°.

$$EtO_2C.[CH_2]_3—CH—CH—CH_2—CO_2Et$$

(IV)

(III)

(V)

(VI)
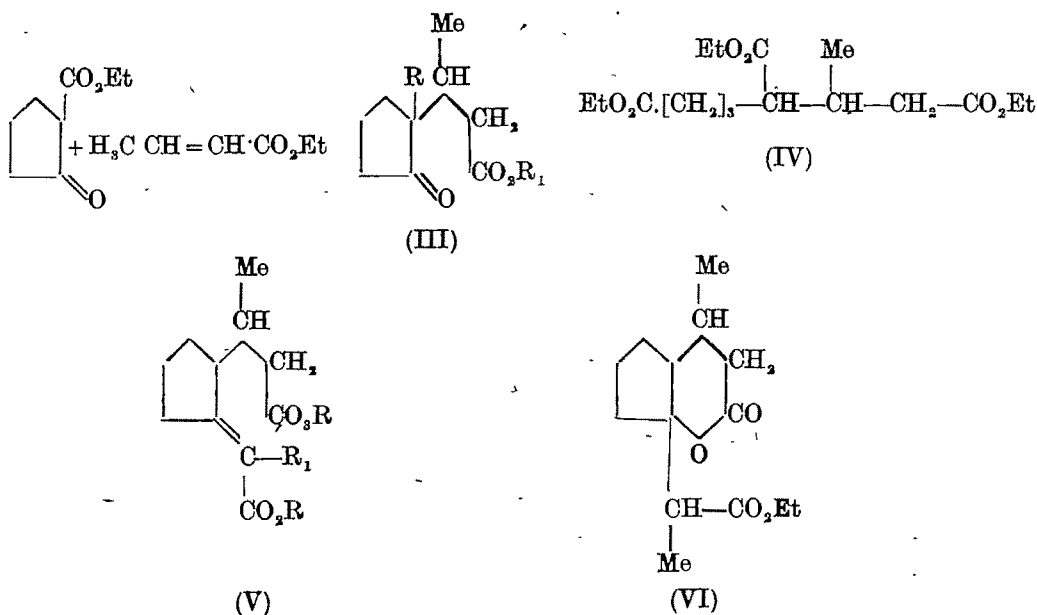
Ethyl cyclo*Pentan-1-one-2-(ethyl-β-n-butyrate)-2-carboxylate.*—A solution of ethyl cyclopentanone carboxylate (15.6 g.) in absolute alcohol (33 c.c.) was added drop by drop to the potassium ethoxide solution (metal, 0.52 g., ether 10 c.c. and alcohol 3 c.c.) cooled in a freezing mixture, when a precipitation of the potassium derivative of the β-ketonic ester was observed. Next a solution of crotonic ester (11.4 g.) in alcohol (12 c.c.) was added very slowly to the well cooled contents of the flask with constant shaking. The whole of the reaction mixture became clear and it was allowed to stand for 7 days. The alcohol was removed under reduced pressure and the residue was acidified with acetic acid and diluted with water when a heavy layer separated at the bottom. The insoluble

oil was extracted with ether, washed three times with water and distilled, b.p. 158-60°/5 mm., yield 18 g. (Found : C, 62.13 ; H, 7.66. $C_{14}H_{22}O_5$ requires C, 62.22 ; H, 8.14 per cent).

The semicarbazone of the above compound was obtained in the usual way as an oil which solidified on standing for several days and crystallised from ethanol, m.p. 112-15°. (Found : N, 13.3. $C_{15}H_{25}O_5N_3$ requires N, 12.84 per cent).

cyclo*Pentan-1-one-2- β-n-butyric Acid.*—The above substituted β-ketonic ester (18 g.) was hydrolysed by refluxing it with hydrochloric acid (100 c.c., 1 : 1) for 16 hours. The mineral acid was removed by evaporation on the water-bath and the residue was distilled, b.p. 154°/4 mm., yield 10 g. The keto-acid failed to furnish a semicarbazone. (Found : C, 63.5 ; H, 8.2. $C_9H_{14}O_3$ requires C, 63.5 ; H, 8.23 per cent).

Ethyl cyclo*Pentan-1-one-2- β-n-butyrate.*—The above keto acid (10 g.) was esterified with a mixture of alcohol (50 c.c.) and sulphuric acid (3 c.c., d 1.84) and the resulting ester was worked up in the usual way, b.p. 117°/4 mm. (Found : C, 66.44 ; H, 8.82. $C_{11}H_{18}O_3$ requires C, 66.66 ; H, 9.09 per cent).

The keto-ester furnished a semicarbazone which was crystallised from dilute methanol, m.p. 138-40°. (Found : N, 16.00. $C_{12}H_{21}O_3N_3$ requires N, 16.47 per cent).

Ethyl 2-Methylhexane-1 :3 : 6-tricarboxylate.—In the above Michael condensation when the temperature was allowed to rise due to lack of care or when, immediately after the addition of unsaturated ester the reaction mixture was removed from the freezing bath, either a mixture of (III, R=CO_2Et ; R_1=Et) and (IV) or exclusively (IV) was obtained by working up the reaction mixture in the usual way. The yield of the reaction product (IV), when exclusively formed, was 90%, b.p. 180°/6.5 mm. (Found : C, 61.2 ; H, 8.4. $C_{16}H_{28}O_6$ requires C, 60.8 ; H, 8.8 per cent).

Ethyl cyclo*Pentan-1-one-2-(ethyl- β-n-butyrate)-5-carboxylate.*—The above compound (IV, 33 g.) was refluxed in benzene (100 c.c.) solution with sodium dust (5 g.) for 3 hours when all the metal went into solution. The reaction product was decomposed with iced hydrochloric acid, extracted with benzene, washed with dilute sodium carbonate solution and water. The benzene layer was dried and distilled, b. p. 156°/1.5-2 mm. The compound furnished a positive ferric reaction and the colour gradually developed through light green, green, deep green to greenish violet. (Found : C, 62.16 ; H, 7.82. $C_{14}H_{22}O_5$ requires C, 62.22 ; H, 8.14 per cent).

The bicarbonate washing was acidified and extracted with ether. The total Dieckmann product (14 g.) was hydrolysed by refluxing with 20% sulphuric acid (60 c.c.) for 24 hours. It was worked up to furnish (III, R=R_1=H).

Ethyl cyclo*Pentylidine-1-cyanoacetate-2- β-n-butyrate.*—A mixture of the keto-ester (III, R=H; R_1=Et ; 23 g.), ethyl cyanoacetate (13 g.), acetamide (5 g.) and glacial acetic acid (100 c.c.) was slowly distilled from a Claisen's flask provided with a fractionating column, the temperature of the distilling vapour being kept between 112° and 115°. When 95 c.c of the distillate were collected another portion of glacial acetic acid (55 c.c) was added and the slow distillation was resumed. After sometime a further quantity of acetic acid (55 c.c.) was colllected as distillate when the distillation was stopped. The residue in the flask was cooled and taken in ether which was washed several times with water, dried and distilled, b.p. 163-70°/7 mm. The unchanged

materials were used in a subsequent lot. The total yield of two such condensations was 2.8 g. The unsaturated cyano-ester consisted of a solid part and a liquid portion. Both gave the same analytical data indicating that the two portions are isomerides. (Found : C, 65.06 ; H, 8.2. $C_{16}H_{23}O_4N$ requires C, 65.52 ; H, 7.85 per cent).

Ethyl cyclo*Pent-1-or 5-ene-1-ethyl methylcyanoacetate* 2- *β-n-butyrate.*—A solution of the above unsaturated ester (2.8 g.) in alcohol (4.5 c.c.) after cooling for 1 hour in a freezing mixture was added to sodium ethoxide solution (metal 2.5 g., alcohol 9 c.c.) which was also cooled in a freezing mixture for the same period of time. The reaction mixture was occasionally shaken during addition and was allowed to cool for another 1 hour and then methyl iodide was poured into it and the mixture immediately refluxed for 5½ hours on the water-bath. The reaction mixture was diluted with cold water and the precipitated oil was extracted with ether and distilled, b.p. 150-70°/7 mm. The product (2.5 g.), thus obtained, was shaken in benzene (3 c.c.) solution with sodium bisulphite solution (20%, 5 c.c.) for 8 hours. It was extracted with ether, dried and distilled, (*i*) b.p. 150-60°/6 mm. (*ii*) 160-70°/6 mm. Both fractions gave the same analytical data. (Found : C, 66.13 ; H, 8.8. $C_{17}H_{25}O_4N$ requires C, 66.45 ; H, 8.14 per cent).

δ-Lactone of cyclo*Pentane-1-(ethyl- α-propionate)-1-hydroxy-2- β-n-butyrate.*—The keto-ester (III, R=H; R_1=Et ; 10 g.) was refluxed in a benzene (25 c.c.) solution with zinc (3.2 g.), ethyl 1-bromopropionate (9 g.) and a crystal of iodine for 1 hour when all the metal went into solution after a vigorous reaction. Then another lot of the metal (3.2 g.), ethyl 1-bromopropionate (3.5 c.c.) and a crystal of iodine was added and the refluxing continued for 45 minutes. Next two lots of zinc (3.2 g.) and a crystal of iodine were added after 1 hour's interval. The Reformatsky's reaction product was decomposed with iced sulphuric acid, extracted with ether, washed with ice-cold 10 per cent caustic soda solution and then with water. The ethereal layer was dried and distilled, b.p. 158-60°/4.5 mm, yield 6 g. (Found : C, 65.98 ; H, 8.55. $C_{14}H_{22}O_4$ requires C, 66.14 ; H, 8.66 per cent).

Ethyl cyclo*Pentylidine-1- α-propionate-2- β-n-butyrate.*—The above lactonic ester (VI, 8.5 g.) was treated with phosphorus pentabromide (1 mole) and left overnight. The clear solution of the reaction mixture was poured into alcohol (50 c.c.), cooled in ice-water. The alcoholic solution was left overnight, diluted with water, extracted with ether, washed with sodium carbonate solution and water. After removal of ether the crude bromo-ester (8 g.) was obtained.

The crude bromo-ester (10 g.) was refluxed for 1½ hours with methanolic caustic potash (10%, 125 c.c.) and to this solution was added aqueous caustic potash (45%, 20 c.c.) and the reaction mixture was refluxed for 2 hours. The alcohol was driven off and the residue was diluted with water and extracted with ether. The clear aqueous solution was acidified with acetic acid and the precipitated heavy oil was extracted with ether. The ether was driven off and the residue was dried under vacuum and esterified with alcohol (50 c.c.) and concentrated sulphuric acid (5 c.c.). The ester was distilled, b.p. 158°/6.5 mm., yield 2 g. (Found : C, 67.5 ; H, 9.16. $C_{16}H_{26}O_4$ requires C, 68.08 ; H, 9.2 per cent).

Ethyl cyclo*Pentane-1-(ethyl- α-propionate)-2- β-n-butyrate.*—The above unsaturated ester was hydrogenated over Adam's catalyst (0.1 g.) in acetic acid (15 c.c.) solution and dis-

tilled, b.p. 160°/9 mm. (Found : C, 67.57 ; H, 9.8. $C_{10}H_{18}O_4$ requires C, 67.6 ; H, 9.85 per cent).

The saturated ester (0.1 g.) was hydrolysed with methanolic caustic potash (10%, 10 c.c.) and worked up in the usual way. A gummy acid was first obtained which crystallised after 8 months. The acid was once crystallised from dilute methanol, m.p. 129-31°.

QUINOLINE DERIVATIVES. PART X

By T. N. GHOSH, A. C. ROY AND S. BANERJEE

For pharmacological study against amoebiasis, iodo and chloro derivatives of 8-hydroxy-5 : 6 : 2' : 3'-pyridoquinoline have been synthesised.

The extensive use of " Chiniofon " and " Vioform " in chronic cases of amoebic dysentery indicates the importance of 8-hydroxy quinoline residue for chemotherapy in amoebiasis. In the search for an ideal amoebicide, it has been thought of considerable interest to synthesise a compound having a pyridine ring fused to 7-chloro- or 7-iodo-8-hydroxyquinoline residue and to study its efficacy in the treatment of amoebic dysentery. In this connection it should be mentioned that some harmol derivatives (that is, compounds having a fused pyridine—indole system) have been found to be active as amoebicidal agents *in vitro* (Pyman *et al.*, *J. Chem. Soc.*, 1929, 2010 ; 1931, 36 ; *Biochem. J.*, 1933, **27**, 727 ; 1934, **28**, 264 ; *Chem. & Ind.*, 1937, **56**, 789).

It has been shown (Ghosh, Banerjee and Laskar, *J. Indian Chem. Soc.*, 1944, **21**, 354) that some hydroxyquinoline derivatives can be prepared directly from the corresponding nitro compounds by applying Skraup's reaction. By taking advantage of this observation, a mixture of 8-hydroxy-5 : 6 : 2' : 3' -pyridoquinoline (I) and 5-nitro-8-hydroxyquinoline has been obtained directly from 2 : 4-dinitrophenol by Skraup's method. The synthesis of the compounds (I) from 5-nitro-8-hydroxyquinoline by Skraup's reaction confirms its structure. On iodination with iodine monochloride or chlorination with chlorine gas, the corresponding 7-iodo- or 7-chloro-derivative (II, R = I or Cl) has been obtained, and is structurally related to " Chiniofon " or " Vioform."

(I)   (II)
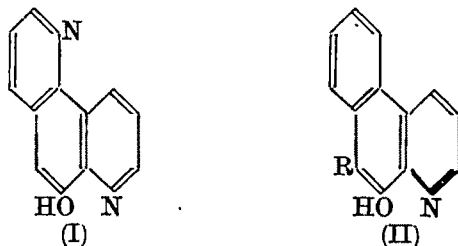
By applying Skraup's reaction to 5-benzeneazo-8-hydroxyquinoline, Matsumura (*J. Amer. Chem. Soc.*, 1930, **52**, 3974) has obtained a mixture of quinoline and a compound to which the structure (I) has been assigned. A comparative study of the derivatives of our compound and those of Matsumura indicates their identity (*vide* experimental). The formation of (I) from the azo compound is now explained on the assumption that concentrated sulphuric acid acts as an oxidising agent towards 5-benzeneazo-8-hydroxyquinoline. Sulphuric acid is thus reduced to sulphurous acid which, in its turn, reduces the above azo derivative to 5-amino-8-hydroxyquinoline which then follows Skraup's reaction. This behaviour of concentrated sulphuric acid has been pointed out in connection with the explanation offered for the formation of hydroxyquinoline derivatives

directly from the corresponding nitro-compounds by Skraup's reaction (*cf.* Ghosh *et al*, *loc. cit.*).

<div align="center">EXPERIMENTAL</div>

8-*Hydroxy*-5 : 6 : 2' : 3' -*pyridoquinoline* (I).—Glycerine (140 g.), made anhydrous by heating at 180° (thermometer in liquid) for 30 minutes, was mixed to a paste by shaking with well powdered 2 : 4-dinitrophenol (50 .g.) to which pure, concentrated sulphuric acid (*d* 1.84, 60 g.) was added dropwise with shaking. The mixture was then heated under reflux on a sand-bath with occasional shaking, when a heavy dark liquid was obtained. As soon as the reaction commenced with frothing and evolution of fumes, the flask was removed from the sand-bath to avoid too vigorous a reaction. After the reaction had subsided, the mixture was heated under reflux on the sand-bath for 2 hours with frequent shaking. The reaction mixture was cooled to room temperature and lumps were broken. Pure, concentrated sulphuric acid (*d* 1.84, 60 g.) was then added dropwise with shaking and the mixture was heated under reflux on the sand-bath for 4 hours more, the flask being removed from the sand-bath when the reaction tended to become vigorous.

Next day the dark mass was taken out of the flask and thoroughly triturated with sufficient quantity of warm water in a mortar. The mixture was filtered and the clear aqueous solution treated with sodium carbonate till distinctly alkaline. A solid was obtained ; this was filtered and washed thoroughly with cold water. It was first crystallised from alcohol (charcoal). The crystalline solid was next triturated with cold 10% hydrochloric acid and the insoluble portion filtered. The clear filtrate was basified with sodium carbonate and the precipitate was filtered, washed with water and dried. It was extracted with ether and after removal of ether, the residue (compound I) was crystallised from alcohol (charcoal) in cream-coloured, slender needles, m.p. 160°-61°, yield 6 g. (Found : C, 73.08 ; H, 4.49 ; N, 14.57. $C_{12}H_8ON_2$ requires C, 73.46 ; H, 4.08 ; N, 14.28 per cent). Matsumura (*loc. cit.*) records m.p. 157-8° for this compound. Its alcohloic solution gives a greenish blue colouration with ferric chloride. The *hydrochloride* was obtained as light yellow rectangular plates, m.p. 274-75°. The *picrate* obtained was thoroughly washed with acetone and was crystallised from a large quantity of alcohol in yellow, rectangular plates, m.p. 237° (decomp.). (Found : N, 16.54. Calc. for $C_{12}H_8ON_2$, $C_6H_3O_7N_3$: N, 16.47 per cent.). The *sulphate* was obtained as a light yellow crystalline powder, m.p. 273° (decomp.). Matsumura records m.p. 237° (decomp.) for the *picrate* and m.p. 273° (decomp.) for the *sulphate* of his compound. Moreover, the analytical figures of his *picrate* correspond with those of ours. These observations indicate that the above compound (I) is identical with that of Matsumura.

The product found insoluble after trituration with 10% hydrochloric acid, as described above, was washed with aqueous sodium carbonate solution and was finally crystallised from alcohol in yellow needles, m.p. 177-78°, yield 1 g. (Found : N, 14.62. Calc. for $C_9H_6O_3N_2$: N, 14.73 per cent). Its identity with 5-nitro-8-hydroxyquinoline was confirmed by a mixed m.p. with a genuine sample.

5-*Nitro*-8-*hydroxyquinoline*.—For the preparation of this compound, according to the method of Kostanecki (*Ber.*, 1821, **24**, 154), 5-nitroso-8-hydroxyquinoline was treated with

well-cooled concentrated nitric acid (4 parts) and the solution was poured into cold water, when a yellow precipitate was obtained, which was filtered and washed with water. Although this compound (m.p. 177-78°) is sparingly soluble in water, it has been found to be the nitrate of 5-nitro-8-hydroxyquinoline, because, when treated with concentrated sulphuric acid, a vigorous reaction takes place with rise in temperature. When cooled and poured into water, a yellow solid was precipitated which was purified through its sodium salt. The solution of the sodium salt in warm water, on treatment with acetic acid, gave 5 : 7-dinitro-8-hydroxyquinoline, m.p. above 280° (Found : N, 18.11. $C_9H_5O_5N_3$ requires N, 17.87 per cent).

When the above nitrate of 5-nitro-8-hydroxyquinoline was triturated with excess of caustic soda solution and the resulting sodium salt was dissolved in warm water and the aqueous solution acidified with acetic acid, a yellow solid was obtained which crystallised from alcohol in yellow needles, m.p. 177-78°. It was proved to be 5-nitro-8-hydroxyquinoline.

Skraup's reaction with 5-Nitro-8-hydroxyquinoline : *Formation of Compound* (I).— The method was the same as mentioned before. The product was crystallised from alcohol (charcoal) and finally from ether in cream-coloured, slender needles, m.p. 160-61°. (Found : N, 14.43. Calc. for $C_{12}H_8ON_2$: N, 14.28 per cent.). Its identity with compound (I) was confirmed by a mixed m.p. and also through its picrate.

7-Iodo-8-hydroxy-5 : 6 : 2′ : 3′ -pyridoquinoline (II, R=I)— To a warm alcoholic solution of compound (I ; 1.7 g.) was added dropwise iodine monochloride (1.9 g.) dissolved in alcohol. Immediately a crystalline compound was precipitated. The mixture was heated on the water-bath at 50-55° for 15 minutes, cooled and then filtered. The solid was triturated with dilute aqueous sodium crabonate solution, filtered and washed with water and then thoroughly with warm alcohol. It is practically insoluble in boiling alcohol and was crystallised from a large quantity of glacial acetic acid in greyish yellow needles, m.p. 217-19° (red colouration), yield 2 g. (Found : I, 38.92. $C_{12}H_7ON_2I$ requires I, 39.44 per cent). When heated with concentrated sulphuric acid, it evolves copious vapour of iodine. When its chloroform solution is shaken with dilute nitric acid, the chloroform layer slowly turns deep violet and the nitric acid turns yellow.

7-Chloro-8-hydroxy-5 : 6 : 2′ : 3′ -pyridoquinoline (II, R=Cl).—The compound (I, 2 g.) was dissolved in dry chloroform and to the cooled solution dry chlorine gas was passed till saturated. A heavy precipitate was obtained, which was filtered and washed with chloroform and ether. The dried solid was treated with water, when a clear solution was obtained which soon deposited a solid. It was filtered, washed with water and was found to be a hydrochloride, m.p. 147-49°. It was well powdered and triturated with concentrated aqueous sodium carbonate solution. A yellowish solid was obtained which was crystallised from alcohol in yellowish rectangular plates, m.p. 253-55°. (Found : Cl, 14.82. $C_{12}H_7ON_2Cl$ requires Cl, 15.40 per cent).

PARACHOR AND RING STRUCTURE. PART V

BY W. V. BHAGWAT AND S. O. SHUKLA

Structural parachors for various groups have been calculated. They are as follows :—

C : CCl—C = 71 ; C : CBr.C = 86 ; C : CI.C = 107.8 ; C : CNO$_2$.C = 89.6 ; C : CNH$_2$.C = 59.9 ; C : COH.C = 46. It is again shown from the study of a large number of benzene derivatives that the parachor for benzene ring may be zero.

Sugden (" Parachor and Valency ", p. 44) in discussing the application of parachor to structural problems suggests that isomerides have almost identical parachors. The observed results (British Association list, 1932) do not favour this view. Variations up to 5 to 6% have been observed in some cases.

Similar variation is shown even by the isomerides formed by substituting the same group in different positions in the same compounds (British Association list, 1932).

Shortcomings of the simple atomic parachors were realised by Mumford and Phillips (*J. Chem. Soc.*, 1928, 155 ; 1929, 2112 ; *Ber.*, 1930, 63, 1818) and Gibling (*J. Chem. Soc.*, 1941, 299) suggested that they should be replaced by group parachors. Although his work is incomplete yet by analogy, the above variation in the case of isomerides can be explained on the ground that the group composition is not identical. It is not necessary to attribute values to ' *n* ' or ' *i* ' substitution as it results in forming different groups.

Ortho-, *meta-* and *para-* isomerides offer an interesting case in which not only atomic but group structures are identical and yet the observed parachor values are not identical. It seems therefore that values for *ortho*, *meta* and *para* positions have to be suggested, in case of ring compounds. But the results available are not enough to make any definite suggestion for the values.

In Part IV (*J. Indian Chem. Soc.*, 1945, 22, 115) it was suggested that the value of benzene ring is either zero or negative. In this paper we have calculated the values for C=CCl.C ; C=CBr.C ; C=CI.C ; C=CNO$_2$.C ; C=CNH$_2$C ; C=COH.C groups on the lines of Gibling (*loc. cit.*). Care has been taken to subtract one benzene ring from another so that no error is allowed to enter due to doubtful value of parachor for benzene ring. The results are as follows.

Method of calculating Group Values.

Benzene   : $P_{obs} = 206$;   E.C. = 0.4.   Hence   S.V. = 205.6.

Chlorobenzene : $P_{obs} = 244.4$; E.C. = 0.6.   Hence   S.V. = 243.8.

Chorobenzene :   S.V. = C$_6$H$_5$Cl = 5C = CHC + C = ClC + P_{ring}.

Benzene S.V. = C$_6$H$_6$ = 6C = CHC + P_{ring}.

Hence chlorobenzene S.V. = Benzene S.V. = 243.8—205.6 = 38.2 = C = ClC—C = CHC. Or C = Cl.C = 38.2 + C=CHC. But C = CHC = 34.3. Hence C = CCl.C = 38.2 + 34.3 = 72.5.

TABLE I

Structural parachor of C=CCl.C *group.*

Difference of compounds.	Difference of groups.	Difference of S.V.	$P_{C\,:\,C.Cl.C.}$
Chlorobenzene – benzene	C=CCl.C—C=CH.C	243.8—105.6	72.5
p-Dichlorobenzene— ,,	2CCCl.C—2C=CH.C	278.7—205.6	70.85
o-Chlorotoluene—toluene	C=C.Cl.C—C=CH.C	280 —245.3	69.0
p-Chlorotoluene—toluene	C=CCl.C—C=CH.C	282.8—245.3	71.8

Structural P for C=C.Cl.C=71.   Average 71.04

TABLE II

Structural parachor of C=CBr.C *group.*

Difference of compounds.	Difference of groups.	Difference of S.V.	$P_{C\,:\,C.Br.C.}$
Bromobenzene—benzene	C=C Br.C—C=CH.C	258.6—205.6	87.3
Bromotoluene—toluene	C=C Br.C—C=CH.C	296 —245.3	85
p-Chlorobromobenzene—benzene	C=C Cl.C+C=CBr.C —2C=CH.C	291.6—205.6	85.6

Structural P for C=CBr.C=86.   Average 86.0

TABLE III

Structural parachor of C=CI.C *group.*

Difference of compounds.	Difference of groups.	Difference of S.V.	$P_{C\,:\,CI.C.}$
Iodobenzene—benzene	C=CI.C—C=CH.C	280.7—205.6	109.4
Iodotoluene—toluene	C=CI.C—C=CH.C	317.6—245.3	106.6
p-Chloro-iodobenzene—benzene	C=C.ClC+C=CI.C— 2C=CH.C	315.4—205.6	107.4

Structural P for C=CI.C=107.8.   Average 107.8

TABLE IV

Structural parachor of C=CNO_2.C *group.*

Difference of compounds.	Difference of groups.	Difference of S.V.	$P_{C\,:\,CNO_2.C.}$
Nitrobenzene—benzene	C=C.NO$_2$.C—C=CH.C	262.6—205.6	91.3
Nitrotoluene—toluene	C=C.NO$_2$.C—C=CH.C	300.1—245.3	89.1
Dichloronitrobenzene—benzene	2C=C.Cl.C + C=C.NO$_2$.C—3C=CH.C	334.3—205.6	89.6
Chlorodinitrobenzene—benzene	2C=C.NO$_2$.C+ C=C.Cl.C—3C=CH.C	348.8—205.6	87.5
Bromonitrobenzene—benzene	C=C.NO$_2$.C+ C=C.Br.C—2C=CH.C	312 —205.6	89
Chloronitrobenzene—benzene	C=C.NO$_2$.C+ C=C.Cl.C—2C=CH.C	299.1—205.6	91

Structural P for C=CNO$_2$.C=89.6.   Average=89.6

TABLE V

Structural parachor of $C=COH.C$ *group.*

Difference of compounds.	Difference of groups.	Difference of S.V.	$P_{C.COH.C.}$
o-Nitrophenol—nitrobenzene	$C=C.OH.C—(C).CH=(C)$	273.25—262.7	44.85
o-Cresol—toluene	$C=C.OH.C—(C).CH=(C)$	256.88—245.4	45.78
o-Hydroxybenzaldheyde—benzaldehyde	$C=C.OH.C—(C).CH=(C)$	267.34—254.36	47.3

Structural P for $C=C.OH.(C)=45.97.$ Average 45.97

TABLE VI

Structural parachor of $C=CNH_2.C$ *group.*

Difference of compounds.	Difference of groups.	Difference of S.V.	$P_{C.C.NH_2.C.}$
Aniline—benzene	$C=C.NH_2.C—(C).CH=(C)$	233.63—205.78	62.15
o-Toluidine—toluene	$C=C.NH_2.(C)—C.CH=(C)$	268.63—245.2	57.73

Structural P for $C=C.NH_2.C=59.94.$ Average 59.94

Application.

The above average values of group parachors are substituted in a large number of compounds and their parachors calculated. These structural values are calculated irrespective of the doubtful value for the parachor of the benzene ring. If benzene ring has any value, the calculated value, when subtracted from the observed value of any benzene derivative, will give this value. The percentage error between the calculated value and observed value with $P_{ring}=0$ falls again within the range of experimental error 0.5% and hence these values again support the view that parachor of benzene ring $=0$. The following typical examples will illustrate this.

TABLE VII

Compound.	S.V.	E.C.	$P_{calc.}$	$P_{obs.}$	Mean diff.
2 Methyl-1 : 4-benzoquinone	276.60	0.70	277.30	272.0	−1.80%
Phenol	219.44	0.42	219.86	220.2—224.8	1.10
Cresol	255.05	0.55	255.60	257.5	0.70
o-Nitrophenol	272.74	0.70	273.44	273.2—274.7	0.10
o-Hydroxybenzaldehyde	267.04	0.60	267.64	268.0	0.10
Aniline	231.04	0.50	231.54	232.7—235.7	0.90
o-Toluidine	269.04	0.67	270.71	269.3	−0.15
Methyl salicylate	321.48	0.95	322.43	322.1—323.7	−0.14

It will be observed that parachors observed in certain cases show a variation of 4 to 5 units. In such cases the mean value varies by 2 to 2.5 units and hence percentage error is high due to unreliability of the results. Otherwise in the majority of the cases percentage error is much less than ± 0.5.

A NOTE ON THE PREPARATION AND PROPERTIES OF SODIUM HYPONITRITE

By Trambaklal Mohanlal Oza

Sodium hyponitrite pentahydrate has been prepared by the method of Divers (*J. Chem. Soc.*, 1899, **47**, 97) modified by Partington and Shah (*ibid.*, 1931, 2071). 2.8622 G. of hydrated substance left 1.5484 g. of anhydrous substance giving off 1.3138 g. of H_2O *i.e.*, $5H_2O$. The analytical results of this substance have been given (Oza, *J. Indian Chem. Soc.*, 1944, **21**, 70).

If nitrogen was not bubbled during the treatment with the amalgam the crystals first obtained from the strong caustic lye consisted of pure Na_2CO_3 and the subsequent lots contained Na_2CO_3 mixed with increasing amounts of $Na_2N_2O_2$ till the fifth crop of crystals, obtained on intensive desiccation, contained pure $Na_2N_2O_2$. The substance, thus formed, was the trihydrate. Another experiment showed that even when nitrogen was bubbled and pure pentahydrate obtained in the normal manner if the mother liquors, containing the hyponitrite, were allowed to stand for a long time (three months) in a vacuum desiccator over sulphuric acid, the crystals formed consisted of pure trihydrate :

(*i*) 2.3005 G. crystals left 1.5229 g. anhydrous substance so that for 106 g. $Na_2N_2O_2$ this is 54.16 g. H_2O *i.e.*, $3H_2O$.

(*ii*) 0.8007 G. crystals left 0.5232 g. anhydrous substance so that for 106 g. $Na_2N_2O_2$ this is 56.2 g. H_2O *i.e.*, $3H_2O$.

The anhydrous substance corresponding to (*i*) and (*ii*) above did not contain any nitrite or carbonate and when analysed by the volumetric method (Oza and Walawalker, unpublished work) was found to consist of pure $Na_2N_2O_2$.

Properties of $Na_2N_2O_2$.—The substance crystallises in beautiful greyish prisms reflecting light at many points. When dehydrated, the crystals crumble to dull white powder. Even a very minute (microscopic) amount of the substance gives a beautiful heavy canary yellow characteristic precipitate with $AgNO_3$. When treated with KI in acidic medium, iodine is not liberated instantaneously as with nitrite but only on standing for a few seconds. This is peculiar since nitrites liberate iodine instantaneously even when present in very very minute amounts.

Resorcinol and periodate have been reported to yield characteristic colour with hyponitrites (Corbet, *Biochem. J.*, 1934, **28**, 1375 ; 1940, **34**, 1029). This has been refuted by Rao (*J. Indian Chem. Soc.*, 1938, **15**, 599) and by Rao and Sastry (*ibid.*, 1942, **19**, 188). A sharp colour change was not observed in this case as well in the mixture of saturated potassium paraperiodate solution and *M/5*-resorcinol (10 c.c. each) on the addition of sodium hyponitrite. The only change noticeable was the transition from the reddish brown colour of the mixture to a more distinctly brownish tinge (p_H of mixture was greater than 9). The test was carefully carried out as there has been a prolonged controversy on its reliability. With pure sodium hyponitrite and potassium paraperiodate, prepared according to Partington and Bahl (*J. Chem. Soc.*, 1934, 1088) having molecular weight of 303.35 (303.2 and 303.5), the colour was noticed over the whole p_H range from strongly

alkaline solution obtained on admixture, to neutral and distinctly acidic range obtained on slow addition of an acid to the mixture. The p_H of the neutral and acidic ranges was determined potentiometrically using quinhydrone-calomel chain. The highest acidity used had p_H of 2.4. The only thing noticed was the development of more and more reddish tinge with increase in acidity of the solution. The original solution of the reagents was reddish, became brownish with alkalinity and again reddish with loss of alkalinity. It was ascertained that in the acid of the concentrations used, the sodium hyponitrite did not all decompose.

A NOTE ON THE ACTION OF ALLYL MAGNESIUM BROMIDE ON LEAD CHLORIDE

K. V. Vijayaraghavan

Lead alkyls were originally prepared by the action of zinc alkyls on lead chloride (Buckton, *Annalen*, 1859, **109**, 222) or by the interaction of sodium-lead alloy and alkyl iodides (Cahours, *Annalen*, 1862, **122**, 67). Pfeiffer and Truskier (*Ber.*, 1904, **37**, 1128) prepared lead tetraethyl by the action of ethyl magnesium bromide on lead chloride. Gruttner and Krause and their collaborators (*Ber.*, 1916, **49**, 141) have prepared a large number of organic compounds of lead using this method. But no attempt seems to have been made to prepare lead tetra-allyl

To the Grignard reagent from 10 g. of allyl bromide, prepared as described by the author (*J. Indian Chem. Soc.*, 1945, **22**, 135) 10 g. (75% of theory) of finely powdered dry lead chloride were added little by little with stirring.

$$4C_3H_5MgBr + 2PbCl_2 \rightarrow Pb(C_3H_5)_4 + Pb + 2MgBr_2 + 2MgCl_2$$

The solution became reddish orange on coming into contact with the lead chloride. This colour immediately disappeared and the whole solution assumed a yellowish tinge. Lead separated as a spongy mass. After all the lead chloride was added, the whole mixture was refluxed for half an hour, and the product decomposed with cold water and extracted with ether. The ethereal extract was dried over calcium chloride. Some yellow powder also separated along with the calcium chloride.

The ethereal solution was coloured yellow. As the ether was being distilled off, a yellowish amorphous solid began to separate. It was filtered off and the distillation continued. The same solid separated again. The ethereal solution contained lead in organo-metallic combination. The compound or compounds formed were unstable and were undergoing spontaneous decomposition. The yellowish solid separating was found to contain organic matter also. It was not merely lead oxide. Pfeiffer and Truskier (*loc. cit.*), Gruttner and Krause (*loc. cit.*) and Jones and Werner have observed a similar phenomenon in the preparation of lead tetraethyl by Pfeiffer's method. Most probably lead diallyl or lead triallyl or both are present in solution due to the incomplete self-oxidation and reduction of lead diallyl, for lead diphenyl and triphenyl are known as strongly coloured substances.

$$2 RMgBr + PbCl_2 \rightarrow R_2Pb + MgBr_2 + MgCl_2$$

$$6 R_2Pb \begin{cases} \rightarrow 4R_3Pb + 2Pb \rightarrow 3R_4Pb + 3Pb \\ \rightarrow 3R_4Pb + 3Pb \end{cases}$$
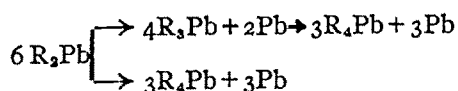
The work was not completed owing to the difficulty of obtaining distillable liquids or crystallisable solids from the ethereal solution.

The author's thanks are due to the late Professor Edward Barnes for suggesting and guiding the investigation.

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COPPER BIGUANIDE CHLORIDE AS A REAGENT FOR THE ESTIMATION OF MERCURY

BY AJITSANKAR BHADURI AND PRIYADARANJAN RĀY

A method for the estimation of mercury has been developed by precipitating it from solution as copper biguanide mercuri-iodide, which, after drying at 105°, can be weighed as $[Cu(BigH^+)_2]HgI_4$; where $BigH$ = one molecule of biguanide, $C_2N_5H_7$.

Equality of cationic and anionic volumes, favourable to their close packing in the crystal lattice, is generally regarded as a primary factor leading to low solubility of ionic compounds, particularly with ions of multiple charges. Their inequality results in a loose packing with considerable interionic gaps providing easy accommodation for solvent molecules. With solvent molecules of high dipole moment like those of water the crystalline structure in the latter case is easily attacked and the substance passes into solution. The solubility of an ionic compound can, therefore, be reduced by eliminating the inequality of its cationic and anionic volumes by suitable co-ordinative addition to the smaller of the two ions. For a substance to be soluble the lattice energy must be overcome by that of the hydration of ions. This is generally expressed by the equation : $-U_0 + H = L$, where U_0 = the lattice energy, H = the heat of hydration and L = heat of solution.

Now a compound with a small cation and a large anion, the lattice pattern will usually consist of a close packing of anions in the interspaces of which the smaller cations are lodged as in the structure of silicates. Such a lattice structure is rather loose due to anionic contact. Hence the strong hydration energy of the small cations might often be enough to break down the structure and to make the substance more or less soluble. On the other hand, if both the cation and anion are equally large they will give rise to a close-packed structure with cation-anion contact increasing the lattice energy. But the hydration energy of large cations, which alone is effective, will be comparatively small. This will, therefore, lower the solubility of the compound.

From theoretical considerations it was expected that metal biguanide cations being of large volume will form very sparingly soluble salts when combined with large anions of the type HgI_4^-, CdI_3^-, etc. This was, in fact, already observed before (Rāy and Ghosh, *J. Indian Chem. Soc.*, 1938, **15**, 347).

With a view to examining whether any of these sparingly soluble salts might be utilised for the estimation of mercury, the present work was undertaken.

From a preliminary examination it was found that copper biguanide mercuri-iodide is very sparingly soluble and can preferably be employed for the estimation of mercury. Reference may be made in this connection to the fact that Spacu and Suciu (*Z. anal. Chem.*, 1929, **77**, 334) effected the quantitative estimation of mercury as copper ethylenediamine mercuri-iodide $[Cu(en)_2](HgI_4)$.

A. BHADURI AND P. RÂY

When copper biguanide chloride (Rây and Bagchi, *J. Indian Chem. Soc.*, 1939, **16**, 617) is added to a dilute solution of mercuric chloride in potassium iodide, rose-coloured prismatic needle-shaped crystals, which are practically insoluble in cold water, separate out. This precipitate, due to its heavy crystalline nature, settles readily and can be filtered quickly through a porcelain gooch or sintered glass crucible. The precipitate is slightly soluble in presence of ammonia or ammonium salts and also in alcohol.

$$K_2HgI_4 + [Cu(BigH^+)_2]Cl_2 = [Cu(BigH^+)_2](HgI_4) + 2KCl.$$
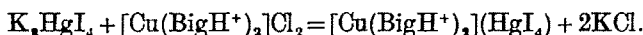
When dried at 105°, the compound has the composition as shown above and contains 20.6% mercury.

<div align="center">EXPERIMENTAL</div>

<div align="center">*Copper Biguanide Mercuri-iodide* $[Cu(BigH^+)_2](HgI_4)$, H_2O.</div>

Preparation.—This was prepared by adding a solution of copper biguanide chloride (Rây and Bagchi, *loc. cit.*) to a dilute solution of mercuric chloride in potassium iodide. The rose-coloured prismatic crystals of the compound were washed with cold water and dried to a constant weight in air. The product when heated to 105° to a constant weight becomes anhydrous. 1.5461G. of the air dried substance lost 0.0281g. in weight at 105°. Percentage of water lost = 1.82. $[Cu(BigH^+)_2](HgI_4)$, H_2O requires 1.84% water.

The dehydrated product on analysis gave Cu, 6.61, 6.58 ; Hg, 20.81, 20.61.

$[Cu(BigH^+)_2](HgI_4)$ requires Cu, 6.53 ; Hg, 20.6 per cent.

Preparation of the Reagent.—For the preparation of the reagent see Rây and Bagchi (*loc. cit.*). A solution of the reagent may also be prepared from copper biguanide sulphate directly by double decomposition with barium chloride. A 1% solution of copper biguanide chloride was used for the estimation.

Conditions of Precipitation.—The success of this method depends chiefly upon the careful observance of the following conditions :

(*a*) *Temperature.*—Since $[Cu(BigH^+)_2](HgI_4)$ has got slight solubility, the estimation should be made at temperatures not exceeding 20°. By precipitating at 33° (room temperature in summer) the result obtained was too low. On the other hand, during the reaction copper biguanide chloride forms copper biguanide iodide which is also difficultly soluble. Since there is always an excess of KI in the solution, too low a temperature may cause the separation of $[Cu(BigH^+)_2]I_2$, giving a high result. The optimum temperature was found to lie between 15° and 20°.

(*b*) *Time.*—It was found that the longer the precipitate was allowed to stand, the better the result obtained. The results were rather low if the precipitate was filtered before the lapse of 4 to 5 hours since its formation.

(*c*) *Volume.*—The total volume of the mixture must be kept between 100 and 200 c.c. according to the amount of mercury present, to ensure complete precipitation. Too small a volume of the mixture, on the other hand, increases the risk of precipitation of $[Cu(BigH^+)_2]I_2$.

(*d*) The *concentration* and *amount* of KI must be restricted to the irreducible minimum, just to keep the mercury in solution as $HgI_4^=$. A 1% solution of KI was found to be most suitable.

(e) A *dilute* solution of the reagent is to be employed to guard against the precipitation of copper biguanide iodide and also in fairly large excess to ensure the complete precipitation of mercury.

(f) *Other conditions.*—The solution must not contain any other anions except those of halogens, as the complex copper biguanide salts of practically all other anions are sparingly soluble. Ammonia and ammonium salts should also be absent, as they have some dissolving action on the precipitate. The precipitation should be made in neutral solution. In the presence of other anions, the latter must be previously removed by precipitating the mercury as HgO.

Method of procedure.—A 1% solution of KI was added to the neutral mercury solution till the yellow precipitate of HgI_2 first formed just redissolved. 10 C.c. more of potassium iodide solution were then added in excess to prevent the separation of any HgI_2 on dilution to 100-150 c.c. hereafter. A 1% solution of the reagent was then added, drop by drop,

TABLE I

Mercury present.	KI added (1% soln.).	Reagent added in 1% soln.	Total vol.	Temp.	Period of of standing.	Wt. of [Cu(BigH⁺)₂] (HgI₄).	Mercury found.	Error.
0.06813 g.	80 c.c.	50 c.c.	150 c.c.	20°	1 hr.	0.3827 g.	0.07884 g.	Copper biguanide iodide simultaneously precipitated.
0.05676	20	13	200	33.5 (room-temp.)	1 hr.	0.1051	0.02165	Incomplete precipitation
0.05243	10	17	150	20	1 hr.	0.2052	0.04229	Do.
0.05676	20	20	200	20	2 hrs.	0.2617	0.05391'	Too low
0.05676	10	30	200	18	2 hrs.	0.2708	0.05580	Low
0.06301	20	18	200	33 (room-temp.)	Overnight	0.2894	0.05962	Too low
0.05961	20	35	125	,,	,,	0.2841	0.05853	Low
0.06131	10	33	200	15	2 hrs.	0.2925	0.06026	Low
0.05846	10	30.9	200	15—20	3 hrs.	0.2827	0.05824	—0.00022
0.06017	10	31.8	200	15—20	3 hrs.	0.2902	0.05978	—0.00039
0.06244	10	33	200	,,	,,	0.3013	0.06207	—0.00037
0.06187	10	32.7	200	,,	4 hrs.	0.2991	0.06162	—0.00025
0.06357	10	33.5	150·	,,	,,	0.3095	0.06377	+0.00020
0.06528	10	34.5	150	,,	,,	0.3157	0.06504	—0.00024
0.09082	10	48	150	,,	5 hrs.	0.4397	0.09059	—0.00023
0.07947	10	42	140	,,	,,	0.3850	0.07932	—0.00015
0.09661	10	49	200	,,	Overnight	0.4718	0.09718 ·	+0.00057
0.06813	10	36	130	,,	5 hrs.	0.3303	0.06805	—0.00008
0.02667	10	15	100	,,	Overnight	0.1295	0.02668	+0.00001
0.1022	10	54	150	,,	,,	0.4971	0.1024	+0.00020

with constant stirring till complete precipitation occurred. It takes some time for the precipitate to appear. An excess of about 20 c.c. of the reagent should be employed.

The precipitate which settles in the form of heavy granular rosy crystals at the bottom of the beaker was allowed to remain at 15-20° for 5 hours or overnight and then filtered through a sintered glass crucible. The precipitate was washed by decantation with a saturated solution of $[Cu(BigH^+)_2](HgI_4)$. When the last drop of the satuarted solution was sucked off, 3 c.c. of ice-cold water were used for washing the precipitate and the sides of the crucible. It was then dried at 105° to a constant weight.

The results of a number of experiments carried out under different conditions are summarised in the above table, from which the optimum conditions for determination, as detailed above, will be apparent. The process offers a very rapid and convenient method of estimating mercury apart from the time allowed for standing. A solution of chemically pure $HgCl_2$ (Scherring-Kahlbaum, *pro analysi* quality) was employed for the estimations. The strength of the solution was also determined by estimating mercury as HgS. In some cases the solid salt $(HgCl_2)$ was directly weighed and used for the estimations.

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NATURAL FLAVONES. PART V. FURTHER OBSERVATIONS ON THE CONSTITUTION OF GARDENIN AND TAMBULIN

By Prafulla Kumar Bose

Gardenin does not couple with diazotised p-nitraniline and its methyl ether is not identical with hibiscetin heptamethyl ether (3 : 5 : 7 : 8 : 3′ : 4′ : 5′-heptamethoxyflavone). Hence gardenin must be formulated as 3 : 6 : 8 : 3′ : 4′ : 5′-hexamethoxy-5-hydroxyflavone. Tambulin dimethyl ether has been found to be identical with pentamethylherbacetin, but not with tangeretin. Hence tambulin is 3 : 8 : 4′-trimethoxy-5 : 7:dihydroxyflavone.

As the result of a detailed examination of gardenin, the colouring matter of Dikamali gum, Bose and Nath (*J Indian Chem. Soc.*, 1938, **15**, 138) advanced two alternative formulae (I and II) for the compound. Based on these structures the dihydroxy-ω-methoxyacetoquinone, obtained by alkaline degradation of gardenin, was assigned the structures (III) or (IV), which can be derived from (I) and (II) respectively.
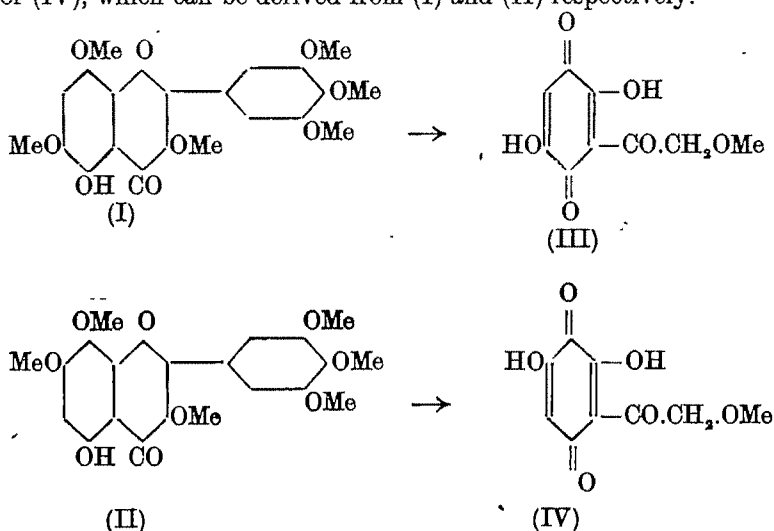
The properties of this quinone, which behaved like a dibasic acid, have been found to be very similar to those of 2 : 5-dihydroxyquinones in general and pedicinin in particular. Pedicinin has been shown to be a quinone having the structure (V) (Bose and Dutt, *J. Indian Chem. Soc.*, 1940, **17**, 499). Based on this analogy the structure (III) appears most plausible for the quinone from gardenin which should consequently be regarded as having the formula (I).

Hydroxyflavones, having a free *para* or *ortho* position to an OH group, are capable of coupling with diazo salts. This property, according to Prof. K. Venkataraman (*private communication*), might be utilised in locating unsubstituted positions in the benzene ring of the pyrone nucleus. An inspection of the formula (I) shows that it has no free positions *ortho* or *para* to the solitary OH group in position 5, whereas formula (II) is expected to

furnish an azo compound in view of the absence of a substituent in position 6. An attempt was therefore made to couple gardenin with diazotised *p*-nitraniline following the procedure described by Mahal and Venkataraman (*Curr. Sci.*, 1938, **6**, 450). Gardenin failed to produce an azo compound. The author therefore felt inclined to assign structure (I) to gardenin.

$$
\begin{array}{cc}
\text{HO}\!-\!\!\!\underset{\text{MeO}}{\overset{\text{O}}{\bigcirc}}\!\!\!-\text{CO.CH:CHPh} & \text{MeO}\,\text{O}\quad\text{OMe} \\
(\text{V}) & (\text{VI})
\end{array}
$$

(V) —CO.CH:CHPh, —OH, HO, MeO, O, O

(VI) MeO O OMe / MeO OMe / OMe / OMe CO
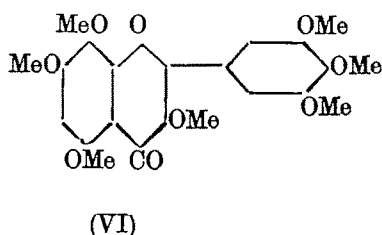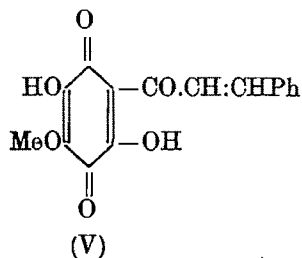
A more convincing proof against formula (II) has now been furnished by Prof. T. R. Seshadri (*private communication*) who has shown that heptamethylhibiscetin (VI) is not identical with methylgardenin. Hence formula (II) for gardenin is ruled out. Gardenin consequently must have the formula (I).

Regarding the constitution of tambulin, the colouring matter of *Xanthoxylum acanthopodium* DC. (Bose and Bose, *J. Indian Chem. Soc.*, 1939, **16**, 183) the formula (VII) was proposed after a careful examination of its properties and degradation products, and after proving that tambulin dimethyl ether is different from tangeretin (Nelson, *J. Amer. Chem. Soc.*, 1934, **56**, 1392). The corroboration of this view has now been made possible

(VII) OMe O / OH, OMe / OH CO, OMe

(VIII) OMe O / MeO, OMe / MeO CO, OMe

(VII)　　　　　　　　　　　　　(VIII)
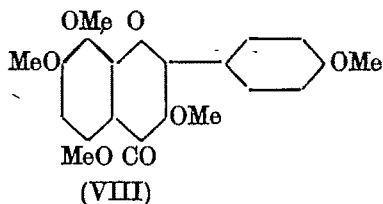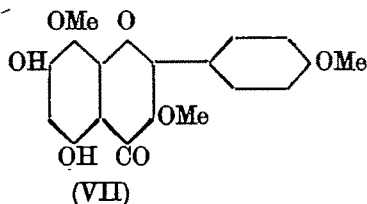
by a direct comparison between herbacetin pentamethyl ether (VIII) and tambulin dimethyl ether. A specimen of the former was placed at our disposal by Professor Seshadri, to whom we offer our best thanks. This ether was found to melt at 157°, and a mixture of this substance and tambulin dimethyl ether (m.p. 160°, after high vacuum distillation) melted at 158-59°. The identity of tambulin dimethyl ether with (VIII) is thus established and consequently tambulin must be formulated as (VII).

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DIPOLE MOMENTS FROM DIELECTRIC CONSTANTS OF LIQUIDS. PART I

By S. R. Phadke, S. D. Gokhale, N. L. Phalnikar and B. V. Bhide

Dielectric constants, refractive indices and densities of a series of several organic substances in the liquid state at different temperatures have been determined. The results are used to calculate the dipole moments of these substances by using Onsager's equation. It has been shown that the moments thus calculated agree within reasonable accuracy with those obtained by other methods.

The determination of dipole moments of molecules involves measurement of dielectric constants in the vapour condition or in solution in a non-polar solvent like benzene. The former method requires intricate technique and can be used only for substances which are easily vaporised without decomposition. The latter method (solution method) is laborious and the results are frequently uncertain due to solvent effects.

Böttcher (*Physica*, 1939, **6**, 50; 1938, **5**, 635) has shown that the dipole moments of many molecules can be obtained easily from a knowledge of the refractive index, density and dielectric constant in the liquid state by the use of Onsager's equation (*i*) (*J. Amer. Chem. Soc.*, 1936, **58**, 1486).

$$\frac{[\epsilon - n^2][2\epsilon + n^2]}{\epsilon[n^2 + 2]^2} = \frac{4\pi}{3} \times N \times \frac{\mu^2}{3KT} \qquad \ldots \quad (i)$$

where ϵ is the dielectric constant, n is the refractive index of the liquid, N is the number of molecules per c.c. *i.e.* $6.023 \times 10^{23} \times d/M$ and μ is the dipole moment.

In the present work the dielectric constants, refractive indices and densities of several liquids have been measured and the dipole moments have been calculated using Onsager's equation (*i*).

EXPERIMENTAL

Materials.—All the substances used in this work were either purchased or prepared by standard methods and carefully purified before use.

Apparatus.—Dielectric constants were measured by the resonance method at 100 meter wave-length. The apparatus used was the same as described by Bhide and Bhide (*J. Univ. Bom.*, 1938, **8**, *iii*, 93) and Ghokhale, Phalnikar and Bhawe (*J. Univ. Bom.*, 1943, **11**, *v*, 56). The experimental condenser was of the same type as described by Bhide and Bhide (*ibid.*, 1939, **9**, *iii*, 220).

Densities were measured by means of a pyknometer and refractive indices were measured with a Bausch and Lomb dipping refractometer. No attempt has been made to find the refractive index at infinite wave-length as was done by Böttcher (*loc. cit.*) because, it has been found that no appreciable error is caused thereby.

The dipole moments of the substances were calculated from the dielectric constants, refractive indices and the densities using Onsager's equation (*i*).

In the following tables the results are summarised along with the moments obtained by using Onsager's equation (*i*) and the values of the moments obtained by the solution method are given from the literature. Values obtained by the vapour method have also been included wherever they are known.

In cases where divergences between the two values obtained by the two methods were observed and where the dipole moments of substances were not previously determined, the moments have been determined using very dilute solutions in benzene, having concentration below 0.01 mol-fraction.

The details of the method used for calculation have been already described (Phalnikar, Bhide and Nargund, *ibid.*, 1941, **10**, *iii*, 48).

Table I gives the relevant data for the moments determined by the solution method.

TABLE I

Substance.	a	β	$P_1{}^e$	P_E	μ
Diethyl azelate	3.1122	0.2270	181.93	63.84	2.41
Diethyl sebacate	3.1603	0.2322	188.18	68.59	2.44
Acetophenone	5.2493	0.2794	216.84	35.55	3.00
Salicylaldehyde	5.7165	0.3479	224.60	27.26	3.13

RESULTS AND DISCUSSION

(In the following discussion dipole moments are expressed in Debye units).

Table II gives the dielectric constants, refractive indices, densities and moments calculated by Onsager's equation (i) and by the solution method, for various esters. Column 8, gives the differences between the moments obtained by two methods and the last column gives references to the dipole moments obtained by the solution method.

TABLE II

Compound.	Temp.	Dielectric constant.	Density	Refractive index.	μ (Ons.)	μ (Sol.)	Diff.	Ref.
Methyl acetate	30°	6.606	0.9083	1.3513	1.729			(1)
	35	6.475	0.9038	1.3494	1.749	1.74	0.009	
	40	6.385	0.8998	1.3477	1.754			
Ethyl acetate*	25	6.4	0.8940		1.83	1.84	0.01	(1)
Butyl acetate	30	4.873	0.8765	1.3827	1.82			(1)
	35	4.801	0.8726	1.3808	1.82	1.85	—0.02	
	40	4.734	0.8686	1.3788	1.83			
*iso*Amyl acetate	30	4.539	0.8500	1.3887	1.75			
	35	4.483	0.8488	1.3871	1.76	1.82	—0.06	(1)
	40	4.414	0.8440	1.3846	1.76			
Ethyl stearate	40	2.958	0.8533	1.4349	1.65			(6)
	45	2.930	0.8498	1.4322	1.65	1.65	0.00	
	50	2.896	0.8422	1.4315	1.65			
Diethyl malonate	25	8.181	1.0488	1.4105	2.58	2.54	0.04	(1)
	30	8.045	1.0425	1.4088	2.55			
Diethyl succinate	30	6.636	1.0285	1.4154	2.37			(1)
	35	6.6656	1.0239	1.4136	2.37	{ 2.28 (gas)		
	40	6.533	1.0190	1.4114	2.39	{ 2.32	0.05	
Diethyl glutarate	30	6.659	1.0144	1.4199	2.46			
	35	6.523	1.0104	1.4181	2.46	2.41	0.05	(1)
	40	6.392	1.0062	1.4154	2.46			
Diethyl azelate	30	5.133	0.9815	1.4284	2.36			
	35	5.047	0.9774	1.4263	2.36	2.41	—0.06	(2)
	40	4.972	0.9738	1.4241	2.36			
Diethyl sebacate	30	4.995	0.9625	1.4255	2.41			
	35	4.925	0.9585	1.4237	2.42	2.43	—0.02	(2)
	40	4.871	0.9539	1.4219	2.43			
Ethoxy ethanol acetate	30	7.567	0.9743	1.4003	2.32			
	40	7.252	0.9664	1.3959	2.32	2.25	0.07	(3)
	50	6.950	0.9586	1.3918	2.31			
Methoxy ethanol stearate	50	3.387	0.8710	1.4364	2.077	2.02	0.05	(3)
Methyl benzoate	30	6.459	1.0796	1.5074	1.83			
	35	6.352	1.0721	1.5032	1.83	1.83	0.00	(1)
	40	6.251	1.0690	1.4987	1.83			
Ethyl benzoate	30	5.991	1.0367	1.4964	1.87			
	35	5.883	1.0324	1.4960	1.87	1.82	0.05	(1)
	40	5.779	1.0279	1.4955	1.87			
Ethyl cinnamate	35	9.4625	1.1143	1.5520	2.09	2.14	—0.05	(1)
	40	9.4193	1.1101	1.5495	2.11			

* Results taken from Bóttcher (*loc. cit.*).

From the above table it will be seen that the dipole moments do not vary appreciably within the temperature range used. This is in accordance with the observation of Böttcher (loc. cit.).

The maximum differences between the dipole moments obtained by the two methods have been found to be 0.06 to 0.09 units. Hence the agreement in the values of the moments is extremely good.

The moment of diethyl succinate obtained by the vapour method is 2.28 to 2.39 (156°-256°) and is in better agreement with the value obtained by the use of Onsager's equation (2.37) than the value obtained by the solution method (2.21).

Table III records the results obtained in the case of some ethers, ketones and aldehydes.

TABLE III

Compound.	Temp.	Dielectric constant.	Density.	Refractive index.	μ (Ons.)	μ (Sol.)	Diff.	Ref.
Anisole	30°	4.314	0.9877	1.5150	1.22	1.16	0.06	(4)
	35	4.261	0.9809	1.5118	1.22			
	40	4.209	0.9761	1.5085	1.23			
p-Bromoanisole	30	7.063	1.4773	1.4741	2.11	2.23	—0.12	(1)
	35	6.971	1.4741	1.4706	2.11			
	40	6.898	1.4716	1.4668	2.13			
Phenetole	30	4.130	0.9616	1.4993	1.27	1.28 (gas)	—0.01	(1)
	35	4.030	0.9598	1.4982	1.27			
	40	3.995	0.9583	1.4971	1.27	1.00	0.27	
Diphenyl ether	30	3.684	1.0610	1.4712	1.13	0.98	0.15	(1)
	35	3.650	1.0551	1.4633	1.15			
	40	3.614	1.0490	1.4591	1.15			
Amyl ether	30	2.636	0.7628	1.3980	1.03	0.97	0.06	(1)
	35	2.602	0.7591	1.3965	1.04			
	40	2.567	0.7543	1.3936	1.05			
Ethylmethyl ketone	30	18.35	0.7965	1.3723	3.2	2.77	0.43	(1)
	35	17.92	0.7930	1.3712	3.2			
	40	17.64	0.7889	1.3696	3.2			
Acetophenone	30	16.86	1.2570	1.5299	3.65	2.97	0.68	(1)
	35	16.67	1.2555	1.5283	3.67			
	40	16.47	1.2501	1.5265	3.67			
Benzophenone	50	12.56	1.0976	1.5484	3.08	3.13	—0.05	(1)
	60	12.23	1.0892	1.5480	3.10			
	65	12.18	1.0851	1.5479	3.08			
Acetone*	10	22.64	0.8020		3.13	2.97 (gas)	0.16	(1)
	20	21.40	0.7910		3.13			
Acetaldehyde*	10	21.80	0.7930		2.74	2.72 (gas)	0.02	(1)

The values for the moments of anisole and diphenyl ether using Onsager's equation have been recently obtained by Jacob, Roberts and Macmillan (J. Amer. Chem. Soc., 1944, 66, 656). The values obtained in the present work agree with their values.

In the case of ethers the variation is small except in the case of p-bromoanisole. The deviation of 0.18 in p-bromoanisole is appreciable and cannot be explained.

* Results taken from Böttcher (loc. cit.).

Among the ketones there is good agreement only in the case of benzophenone, while in ethylmethyl ketone, acetophenone and acetone the deviations are very high. In the case of acetone the deviation may be attributed to the enolic nature leading to association like in other hydroxy compounds.

Table IV gives the results obtained in the case of different types of compounds such as nitroaniline, nitrochlorobenzenes etc.

TABLE IV

Compound.	Temp.	Dielectric constant.	Density.	Refractive index	μ (Ons.)	μ (Sol.)	Diff.	Ref.
p-Nitroaniline	160°	56.27	1.1786	1.5401	7.09	7.1	—0.01	(1)
	170	55.61	1.1413	1.5229	7.14			
	180	55.06	1.1192	1.5130	7.24			
o-Nitroaniline	90	34.530	1.1991	1.5431	4.97	4.72	0.25	(5)
	100	34.160	1.1682	1.5562	5.00			
	110	33.962	1.1336	1.5232	5.03			
m-Chloronitro benzene	55	13.95	1.1761	1.4771	3.22			(1)
	60	13.61	1.1293	1.4553	3.32	3.38	—0.06	
	65	13.29	1.0912	1.4416	3.40			

The nitroanilines have comparatively high melting points. The variation of dipole moments with temperature in these cases is of the order of 0.1 unit which may be attributed to experimental errors because at such high temperatures accurate measurements of densities are difficult.

The agreement between the values of moments by the two methods for the compounds listed above is satisfactory.

From the above discussion it will be seen that the dipole moments calculated by the Onsager's equation in the case of esters, aldehydes, ketones, ethers etc. are in agreement with the values obtained by the solution method. This is in agreement with the conclusions of Böttcher (loc. cit.) and Jacobs et al (loc. cit.).

Wilson (Chem. Rev., 1939, 25, 377) has criticised Böttcher's calculations and is of the opinion that this agreement is theoretically surprising and is probably due to fortuitous cancellation of errors. In spite of this remark, the method appears to give correct moments and can be safely relied on and used at least as an empirical equation.

The following is a list of references for dipole moments obtained by solution or gas method taken from literature and referred to in the last column of the tables used in the above discussion.

(1) Table of Dipole Moments. Trans. Faraday Soc., 1934.

(2) Present work.

(3) Gokhale, Phalnikar and Bhawe. J. Univ. Bom. 1943, 11, v, 56.

(4) Roberts, MacMiller and Jacob, J. Amer. Chem. Soc., 1944, 66, 657.

(5) Kubo, Sci. Papers Inst. Phys. & Chem. Research Tokyo, 1935, 26, 242.

(6) From analogy with other aliphatic esters.

DIPOLE MOMENTS FROM DIELECTRIC CONSTANTS OF LIQUIDS. PART II

By S. R. PHADKE, N. L. PHALNIKAR AND B. V. BHIDE

Dielectric constants, refractive indices and densities of a series of substances likely to contain a hydrogen bond have been measured at different temperatures and the moments calculated by using Onsager's equation. The values of dipole moments of substances forming intermolecular bonds show large deviations from values obtained by other methods. On the other hand the values of moments of substances forming an internal hydrogen bond agree with those obtained by other methods. Evidence of internal hydrogen bond has been supplied by determination of molecular weights cryoscopically.

In Part I the dipole moments of a number of non-associated compounds have been determined from their dielectric constants and the applicability of Onsager's equation to such a calculation has been proved. In this paper the dipole moments of a number of compounds likely to form a hydrogen bond have been calculated using the same method.

EXPERIMENTAL

Materials.—All the substances used were either purchased or prepared by standard methods and purified before use. The apparatus and the method of calculation have been described in Part I and the moments are expressed in Debye units.

RESULTS AND DISCUSSION

Three types of hydrogen bonding may be distinguished amongst organic compounds.

(1) Intermolecular hydrogen bond resulting in ' unlimited association ' and forming chain-like molecules, as in alcohols, phenols, water, etc.

(2) The inter-molecular hydrogen bonding leading to a definite dimer formation as in carboxylic acids.

(3). Intramolecular hydrogen bonding formed by the presence of strong electro-negative substituents in close proximity to the hydrogen atoms. This type of compounds is also called chelated compounds. Salicyladehyde, o-chlorophenol, o-nitrophenol etc. are examples of this type.

The following table records the results for compounds containing intermolecular hydrogen bond.

TABLE Ia

Substances containing intermolecular hydrogen bond.

Substance.	Temp.	Dielectric constant.	Density.	Refractive index.	μ (Ons.)	μ (Sol.)	Diff.	Ref.
Water	25°	83.2	0.9995		3.11	1.84	1.84	1
Primary alcohols								
Methyl alcohol	20	34.0	0.792	1.324	3.01	1.69	1.32	3
Ethyl alcohol	20	23.8	0.789	1.361	2.92	1.67	1.25	3
,, ,,	70	17.6	0.7456		2.84			1
n-Propyl alcohol	20	22.2	0.804	1.386	3.09	1.58	1.51	3
n-Butyl alcohol	20	17.4	0.8098	1.3992				3
,, ,,	30	15.683	0.7943	1.3955	2.93	1.7	1.23	
isoButyl alcohol	30	15.691	0.8083	1.3869	2.93	1.7	1.23	
n-Octyl alcohol	20	10.34	0.8253	1.430	3.02	1.7	1.32	3
Ethylene glycol	20	38.8	1.115	1.4318	3.49	2.28	1.21	3
Propylene glycol	20	32.0	1.038	1.4323	3.63	2.25	1.38	3
Trimethylene glycol	20	35.0	1.053	1.4396	4.21	2.5	1.71	3
Ethylene glycol monomethyl ether	30	15.95	0.9532	1.3977	2.74	2.2**	0.54	
Ethylene glycol mono-acetate	30	12.95	1.0965	1.4150	2.63	2.34**	0.29	

*These values have been taken from Gokhale, Phalnikar and Bhawe (*J. Univ. Bom.*, 1943, 11, v, 56).

TABLE Ib

Secondary alcohols

Substance.	Temp.	Dielectric constant.	Density.	Refractive index.	μ (Ons.)	μ (Sol.)	Diff.	Ref.
cycloHexanol	30°	14.737	0.9554	1.4579	2.83	1.9	0.93	3
	35	14.147	0.9507	1.4565	2.83			
	45	12.531	0.9411	1.4532	2.83			
o-Methylcyclo-hexanol	30	11.040	0.9260	1.4563	2.56	1.95	0.61	
	35	10.040	0.9247	1.4550	2.49			
	40	9.239	0.9222	1.4539	2.37			
m-Methylcyclo-hexanol	30	11.633	0.9131	1.4538	2.5	1.89	0.61	
	35	11.032	0.9113	1.4524	2.48			
p-Methylcyclo-hexanol	30	11.992	0.9111	1.4532	2.7	1.87	0.83	
	35	11.481	0.9088	1.4524	2.66			
o-Cresol	25	11.479	1.0315	1.5353	2.32	1.48	0.84	
	30	10.937	1.0281	1.5334	2.28			
m-Cresol	25	11.749	1.0175	1.5294	2.38	1.6	0.78	
	30	11.237	1.0145	1.5273	2.35			
Methyl heptanol	20	3.37	0.8348		1.26	1.62	1.36	2

TABLE Ic

Teritary alcohols

Substance.	Temp.	Dielectric constant.	Density.	Refractive index.	μ (Ons.)	μ^* (Sol.)	Diff.	Ref.
Tertiary butyl alcohol	20°	10.9	0.777	1.3878	1.74	1.65	0.09	3
Tertiary amyl alcohol	30	6.695	0.8081	1.3932	1.94	1.83	0.11	
	40	6.443	0.8084	1.3906	1.93			

Some of the above results have been collected from literature for the purposes of calculation. The number in the last column refers to the following references :—

    1. Böttcher, *Physica*, 1938, 6, 635.

    2. Smyth and Stoops, *J. Amer. Chem. Soc.*, 1929, 51, 3310.

    3. Morgan and Yager, *Ind. Eng. Chem.*, 1940, 82, 1519.

*Values of the moments by the solution method have been taken from the table of Dipole moments, *Trans. Faraday Soc.*, 1934.

It will be seen from the table given above that in the case of water and other primary alcohols the moments obtained by the Onsager equation are approximately 3, while those obtained by the solution method are about 1.6 to 1.9. The difference in the values of the moments obtained by the two methods is 1.2 to 1.5.

The cyclohexanols and cresols are included as secondary alcohols. The cresols will behave as secondary alcohols because of resonance. In the case of these secondary alcohols the difference in the values of moments obtained by the solution method and the Onsager equation are 0.7 to 0.9 units higher as contrasted with 1.2 in the case of primary alcohols.

The case of tertiary alcohols is very interesting. Here the moments obtained by both the methods agree very well.

These differences can be very well accounted for if the nature of association is taken into account. In the primary alcohols the intermolecular hydrogen bond leads to unlimited association and formation of chain-like molecules. The resultant dipole moment of such chain-like molecules will depend upon the extent of association and the valency angles. Generally in the liquid condition the moments of such chain-like molecules will be higher than those for the simple molecules.

In a solution of these compounds in a non-polar solvent the hydrogen bond will be broken and hence the compound will be split up into normal molecules. The moment determined by the solution method will therefore be generally lower than that determined by the Onsager method as has been observed.

In the secondary alcohols the intermolecular hydrogen bond will be present but the extent of association here will be less than that in primary alchols. The moments obtained by the two methods will not be the same, but the difference will be less than that in the case of primary alcohols as the extent of association is less.

The moments obtained by the two methods in the case of tertiary alcohols agree and are not vitiated by the presence of hydroxylic group. This is due to the fact that intermolecular hydrogen bond formation is prevented in tertiary alcohols due to steric hindrance. In tertiary amyl and butyl alcohols for example, the hydroxylic group being surrounded by three alkyl groups the chain forming tendency is hindered.

The spectroscopic examination of tertiary compounds supports this view. The spectroscopic examination of amyl alcohols (Badger and Bauer, *J. Chem. Phys.*, 1937, **5**, 843, 852) shows appreciable absorption characteristic of monomer in addition to broad polymer bands in the liquid condition. This monomer absorption is greatest in tertiary alcohols, decreases with a secondary one and is the least with the primary alcohols. The formation of chain-like associated molecules, a characteristic of primary alcohols and to a lesser extent in secondary alcohols, is not possible in the case of tertiary alcohols due to steric hindrance.

It may be noted that the greatest association in primary and secondary alcohols results in abnormal properties such as abnormal molecular weights, parachor, boiling points etc.

The following table gives the molecular weights of some of these compounds determined crysocopically in benzene. Column two of the table gives the molecular weights actually obtained and column three, the formula weights.

TABLE II

| Compound. | Molecular weight | |
	obs.	calc.
m-Cresol	124	108
*cyclo*Hexanol	119	100
o-Methyl *cyclo*hexanol	137	114
m-Methyl *cyclo*hexanol	139	114
p-Methyl *cyclo*hexanol	140	114
o-Chlorophenol	128	128.5
p-Chlorophenol	134	128.5
o-Nitrophenol	138	139.0

It will be seen that the first five compounds (belonging to the secondary alcohol type) show abnormal molecular weights even in dilute benzene solutions, a characteristic of intermolecular hydrogen bonding liquids. *o*-Chlorophenol and *o*-nitrophenol show normal molecular weights in benzene solutions as these substances form intra-molecular hydrogen bonds, *p*-chlorophenol on the other hand shows a higher molecular weight as it can form a weak intermolecular hydrogen bond (*cf.* Pauling, *loc. cit.*).

The following table gives the results obtained in the case of a few *intra*-molecular hydrogen bonding liquids.

TABLE III

Substance.	Temp.	Dielectric constant.	Density.	Refractive index.	μ (Ons.)	μ (Sol.)	Diff.	Ref.'
o-Chlorophenol	30°	6.163	1.2382	1.5475	1.56	1.43	0.11	(1)
	35	6.0626	1.2297	1.5446	1.53			
	40	5.914	1.2239	1.5429	1.55			
p-Chlorophenol	55	9.358	1.2663	1.5419	2.12	2.27	0.13	(1)
	60	9.165	1.2629	1.5388	2.10			
	65	8.983	1.2563	1.5361	2.08			
o-Nitrophenol	50	17.342	1.2823	1.5723	3.01	3.10	0.09	(1)
	55	17.025	1.2765	1.5708	3.01			
	60	16.703	1.2712	1.5690	3.01			
Salicylaldehyde	30	17.091	1.1654	1.4701	3.08	3.13	0.05	(2)
	35	16.658	1.1606	1.4680	3.07			
	40	16.374	1.1569	1.4661	3.05			
Methyl salicylate	30	9.443	1.1738	1.4299	2.33	2.41	0.08	(1)
	35	9.316	1.1684	1.5266	2.34			
	40	9.129	1.1635	1.5240	2.35			
Ethyl salicylate	30	7.99	1.1190	1.5070	2.80	2.88	0.08	(1)
	35	7.881	1.1145	1.5041	2.83			
	40	7.793	1.1107	1.5002	2.85			

The following is a list of references for dipole moments obtained by solution or gas method, taken from literature and referred to in the last column of the tables used in the above discussion.

(1) Table of dipole moments, *Trans. Faraday. Soc.*, 1934.

(2) Present work, Part I of this series.

From the table above it will be observed that the moments obtained by the Onsager equation and those obtained by the solution method do not differ much in the case of chelated compounds.

All these compounds, (excepting p-chlorophenol) have a tendency towards chelation. The presence of strong *intra*-molecular hydrogen bond in these liquids is indicated by their absorption spectra (Pauling, " Nature of the Chemical Bond," p. 323, Cornell University Press).

In the case of o-chlorophenol there is also a tendency to form dimers but this tendency will always be suppressed by the presence of the *cis*-form of o-chlorophenol constituting 90 per cent. of the substance (Pauling, *loc. cit.*). Spectroscopic examination of o-chlorophenol shows that this *cis*-form is present to the extent of 90% in the liquid.

In the chelated compounds there is no intermolecular bond both in the liquid condition or in solution in a non-polar solvent. Hence the moments obtained by the Onsager equation, *i.e.* in the liquid condition or by the solution method will not be different, a fact borne out by experiments.

In p-chlorophenol there will be a tendency to form dimers but the results as compared with other chelated compounds show that in p-chlorophenol the dimer formation is small.

CONCLUSION

The Onsager equation gives correct values for dipole moments of liquids which are not associated. Abnormally high values of dipole moments are obtained generally in the case of hydroxyl compounds which form indefinite chain polymers in the liquid condition due to the formation of hydrogen bonds. The equation, therefore, can be safely used to calculate the dipole moments from the dielectric constants of liquids excepting the associated liquids.

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THE THERMAL DECOMPOSITION OF SODIUM AND POTASSIUM NITRITES. PART II. ACTION OF NITRIC OXIDE, OXYGEN AND NITROGEN PEROXIDE ON THE FUSED NITRITES

By Trambaklal Mohanlal Oza and Bhasker Ramakrishna Walawalkar

It is found that (*i*) nitrogen is produced by the action of nitric oxide on the fused nitrites ; (*ii*) nitrogen peroxide in becoming reduced to nitrogen passes through the stage of nitric oxide ; (*iii*) the nitrogen peroxide formed in the initial reversible stage by the dissociation of the nitrites reacts simultaneously with the produced alkali oxide and the nitrite in the residue, and (*iv*) the decomposition of alkali nitrites appears to be a case of homogeneous reactions proceeding to a very considerable extent, only in the molten mass. The mechanism of the reactions is discussed and formulated.

In Part I of this work it has been shown that sodium and potassium nitrite undergo decomposition in the initial stage as

$$4KNO_2 \rightleftharpoons 2K_2O + 2NO + 2NO_2$$

and evidence has been obtained tending to explain the disappearance of nitrogen peroxide and appearance of nitrogen in the gas and nitrate in the residue. In this part further light is thrown on these and on the nature of the decomposition, more especially, on the mode of production of nitrogen.

The action of nitric oxide and nitrogen peroxide on sodium and potassium nitrite has been studied by Oswald (*Ann. Chim.*, 1914, 9, 32) who found that (*i*) nitric oxide did not act upon the nitrites till the latter decomposed and (*ii*) nitrogen peroxide reacted with them to produce both nitric oxide and nitrogen. He deduced that nitrogen was produced from nitrogen peroxide in a single step as :

$$4KNO_2 + 2NO_2 \longrightarrow 4KNO_3 + N_2$$
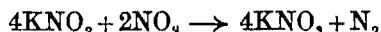
On the other hand, Mehta (M.Sc., thesis abstract, *J. Univ. Bom.*, 1941, 135) who studied the action of nitric oxide and nitrogen peroxide on potassium and silver nitrites, states that (*i*) nitrogen peroxide, produced from the nitrites in the initial stage, reacts with both the alkali oxide simultaneously produced and with the undecomposed nitrite producing nitric oxide in the latter case : evidence for this has already been adduced in Part I (*J. Indian Chem. Soc.*, 1945, 22, 173) ; (*ii*) nitrogen is produced by the action of nitric oxide on the nitrite in the reacting mass.

In this paper the results of streaming at a steady rate, measured volumes of nitric oxide and oxygen are described. Oxygen has been used in place of nitrogen peroxide since the latter cannot be conveniently measured and the results have been confirmed by using pure nitrogen peroxide itself. Experiments have also been described to throw light on the particular part played by the alkali oxide (in the residue) in the reactions and on the general nature of the reactions.

EXPERIMENTAL

Materials.—Sodium and potassium nitrites were the same as those used in Part I.
Nitric oxide.—Nitric oxide was prepared from $FeSO_4$, H_2SO_4, and KNO_3. It was

first collected in an inverted bottle over air-free water and then carefully transferred, after drying over a long layer of P_2O_5, to the evacuated reservoir with the help of a manometer. The gas was tested for purity; three samples gave the same results : e.g., 53.58 c.c. left 1.27 c.c. unabsorbed in alkaline Na_2SO_3 followed by acidified $FeSO_4$. The results in Table I are corrected for this impurity.

Oxygen.—Oxygen was prepared by heating $KClO_3 + MnO_2$ kept in a tube sealed on to the 4th way of the 4-way tap, T, in the apparatus (vide fig. Part I) previously evacuated and tested for leaks. The first few litres were pumped off and the subsequent lot collected for the experiments. On absorption in alkaline pyrogallol a very tiny bubble was left unabsorbed from about 25-30 c.c. of the gas.

Nitrogen peroxide.—Nitrogen peroxide was prepared by heating finely powdered $Pb(NO_3)_2$. The gases generated on heating were led into a U-tube immersed in a freezing mixture of ice and $CaCl_2$. When sufficient amount of the solid (dirty greenish) was collected, heating was discontinued, the solid allowed to liquefy and evaporate freely if necessary under partial vacuum. The liquid became colourless in course of time which was then again frozen to white mass and the gas transferred to the evacuated and tested reservoir by means of the apparatus shown in Fig. 1. Samples of the gas were absorbed in KOH in the apparatus (vide fig. Part I) and the KOH, analysed for nitrite and nitrate, gave equivalant amounts of the two.
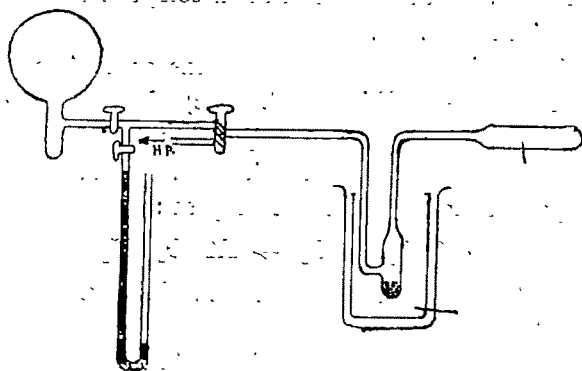
FIG. 1

Procedure.—The apparatus used and the method of work were the same as described in Part I. The measuring burette was dispensed with in experiments with nitrogen peroxide. The recorded volumes are all at N.T.P. For the same reason as stated in Part I, results of solid residue analysis in Tables I, II, and III are approximate.

The results of experiments with nitric oxide are given in Table I.

TABLE I

Nitric oxide as the streaming gas

Substance.	Temp.	Total passed.	Gas obtained.	Compn. of gas N_2O_3 (in K)	NO.	N_2.	Residue (g.) NO'_3.	NO'_2.	O''.
$NaNO_2$	380°	53.58 c.c.	55.77 c.c.	2.07	0	0.0	0.00	0.9900	0.0044
KNO_2	410	53.50	56.68	2.47	(apparently)	0.93	0.01075	0.9575	0.0185
KNO_2	460	59.19	62.87	3.30	—	1.26	0.01775	0.9360	0.0262

These results show that (i) nitrogen trioxide alone, unmixed with nitric oxide or nitrogen, in the gas and nitrate in the residue, is produced with sodium nitrite even at 380°. This is in line·with the corresponding result with nitrogen as streaming gas (Part I) ; (ii) with potassium nitrite, on the other hand, all the three gases, viz., nitric oxide, nitrogen peroxide and nitrogen and also nitrate, are produced, their quantities increasing with temperature ; (iii) the volume of nitrogen is greater than what corresponds to reduction in the volume of nitric oxide passed : this shows that the nitrogen was not all produced merely by the reduction of the streamed nitric oxide, i.e., some of it was necessarily produced from the decomposing nitrite.

If the results in this table are compared with the results in Table I (Part I) it can be inferred that the decomposition of the fused nitrites is retarded by the presence of nitric oxide in the system. This fact lends support to the reversible nature of the initial stage in the decomposition.

TABLE II

Oxygen as the streaming gas

Substance,	Temp.	Total passed.	Gas obtained.	O_2 used up.	Gas produced (o.c.)	Compn. of gas			Residue (g.)		
						NO_2 (in K)	NO.	N_2.	NO_3'.	NO_2'	O''.
NaNO$_2$	330°	53.67	51.5	3.7	11.26	9.8	0.0	1.46	0.0167	0.9570	0.0133
NaNO$_2$	380	54.7	53.5	2.6	12.36	10.98	0.0	1.38	0.0165	0.9550	0.0143
KNO$_2$	410	53.19	52.28	1.8	16.57	15.7	0.0	0.87	0.2000	0.9380	0.0263
KNO$_2$	460	55.03	52.23	5.5	22.87	20.1	0.0	2.77	0.0490	0.9040	0.0303

The results of experiments on the streaming of oxygen are given in Table II. These results show that (i) the quantity of nitric oxide decomposed is comparatively high than in corresponding experiments with nitrogen or nitric oxide ; the quantities of oxide and nitrate in the residue are comparatively large showing that the formation of these goes hand-in-hand with the decomposition ; (ii) the amounts of nitrogen formed in these experiments, as compared with those formed in experiments with nitric oxide, (and also with nitrogen, Part I), are greater and it is very interesting to observe that the amounts of nitrogen formed appear to be related to the amounts of oxygen used up* · and to the amounts of nitrate formed. It would thus appear that nitrate production and nitrogen production are related to the reactions consuming oxygen ; (iii) more nitrate is produced in experiments with KNO$_2$ than with NaNO$_2$ showing that the former reacted in preference to the latter with the oxides of nitrogen ; (iv) the amounts of nitrogen peroxide produced in the alkali are fairly large thus showing that a large quantity of nitric oxide is produced in these experiments.

* Oxygen used up (column 5, Table II) is found by subtracting the volume of nitrogen from the gas obtained and subtracting the result from the total oxygen passed.

3—1547P—8

The production of large quantities of nitrogen peroxide and the consumption of oxygen could be explained on the supposition that nitrogen peroxide is becoming reduced to nitrogen only in stages through the intermediate production of nitric oxide and *not* directly in one stage. The nitric oxide, produced in the decomposition (or, dissociation) takes up oxygen and forms nitrogen peroxide ; the latter reacts with the nitrite and becomes reduced to nitric oxide ; the reformed nitric oxide again takes up oxygen to form nitrogen peroxide and so on, the reactions consume oxygen and form nitrate. The simultaneous increase in nitrogen production receives explanation on the greater frequency of contacts of nitric oxide with the nitrite.

The results of experiments with nitrogen peroxide as streaming gas are given in Table III.

TABLE III

Nitrogen peroxide as the streaming gas

Substance.	Temp.	Total gas obtained.	KNO_3 in alkali (K)	KNO_2 in alkali	Compn. of gas N_2O_3 NO (absorbed in K)		N_2	Residue NO_3'	NO_2
$NaNO_2$	330°	34.66 c.c.	0.1810 g.	0.0600 g.	6.25	28.25	0.16	0.0154	0.9875
$NaNO_2$	380	36.57	0.202	0.0530	10.5	25.25	0.82	0.0338	0.9725
KNO_2	410	34.34	0.1850	0.0553	8.2	24.7	1.44	0.0260	0.9780
KNO_2	460	42.66	0.2314	0.0646	11.34	28.5	2.82	0.0570	0.9572

It will be seen that these results are quite comparable with those in Table II   They receive explanation also on similar lines. It is significant that the amount of nitrogen produced in experiments with KNO_2 and oxygen or nitrogen peroxide are quite comparable though this is not the case with $NaNO_2$. Ostwald (*loc. cit.*) found that nitric oxide did not act upon the nitrites till the latter decomposed while nitrogen peroxide did. If therefore nitrogen production was directly obtained by the reduction of nitrogen peroxide with the nitrite, comparable production of nitrogen should be observed in all these experiments. The results thus indirectly conform to the view already deduced from the experimental results of Table II and inferred from the results of experiments with MgO (Part I) that the nitrogen production does not result from nitrogen peroxide in one step. On the other hand, if the production of nitrogen depended upon the reduction of nitric oxide, then, since nitric oxide reacts with the nitrite only at higher temperatures, its production in the case of potassium nitrite and lack of production in the case of sodium nitrite find ready explanation.

The results may now be recapitulated with advantage. The facts recorded in Part I, substantiated by the additional evidence adduced in this part, show convincingly that the initial stage in the decomposition is the dissociation of the nitrites as

$$4MNO_2 \rightleftharpoons 2M_2O + 2NO + 2NO_2 \qquad \dots \quad (1)$$
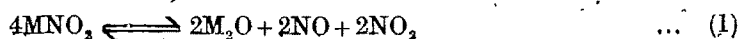
nitrogen and nitrate being produced in a subsequent stage. The facts that (i) nitrogen is produced in experiments with nitric oxide—a gas which acts on the nitrites only at higher temperatures; (ii) very large excess of nitrogen is not produced in experiments with oxygen or nitrogen peroxide which (latter) is known to act as oxidizing agent at much lower temperatures than does nitric oxide, show that nitrogen is produced by the reduction of nitric oxide. The evidence recorded in Part I (e.g. experiments with MgO) substantiates the same view. Thus, nitrogen is produced by the action of nitric oxide on the fused nitrites, as

$$2MNO_2 + 2NO \longrightarrow 2MNO_3 + N_2 \qquad \qquad \dots (2)$$
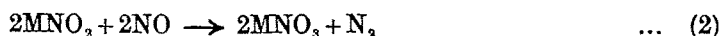
Oza and Shah (J. Univ. Bom., 1942, 11, 56) found that (i) gaseous products of the decomposition contained, in the initial stages, a very large proportion of nitric oxide and (ii) in none of the experiments was nitric oxide obtained unmixed with nitrogen. In view of (a) the now established nature of the primary stage in the decomposition (1), (b) great vigour of the reaction when the nitrites, mixed with MgO, undergo fusion and (c) the fact that the gaseous products in (b) consist of almost pure nitric oxide, the observation (i) of Oza and Shah receives explanation on the well known behaviour of nitrogen peroxide to oxides of alkali metals, as,

$$M_2O + 2NO_2 \longrightarrow MNO_2 + MNO_3 \qquad \qquad \dots (3)$$
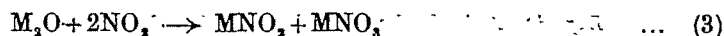
Such a behaviour, if quantitative, would consume half the alkali oxide and all nitrogen peroxide produced in (1) and the residue will still continue to indicate free alkali and will show the presence of nitrate while the gaseous products will contain only nitric oxide. Since, however, nitric oxide unmixed with nitrogen, has never been isolated, it would appear that the reactions (3) and (2) proceed hand-in-hand. Experimental facts (Table III) indicate that nitrogen peroxide can react with potassium nitrite also as

$$MNO_2 + NO_2 \longrightarrow MNO_3 + NO \qquad \qquad \dots (4)$$
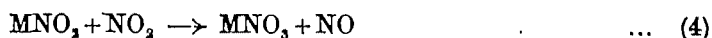
and it is therefore not unlikely that this reaction, too, may be proceeding side by side with reactions (2) and (3). The available experimental evidence as to the quantitative nature of the gaseous products and the residue could be explained both on reactions (2) and (3) or on (2), (3) and (4) following the primary stage (1).

A close observation into the above equations (1), (2), (3) and (4), can enable us to decide what actually happens. For, while there are two nitrogen peroxide consuming reactions (3 and 4) there is only one reaction (eqn. 1) producing and only one (3) consuming, the alkali oxide. Hence if the nitrogen peroxide reacted quantitatively, only with the alkali oxide according to (3), the amount of the oxide left in the residue should be given by the equation :

$$3MNO_2 \longrightarrow M_2O + MNO_3 + 2NO \text{ (summing up 1 and 3)} \qquad \dots (5)$$
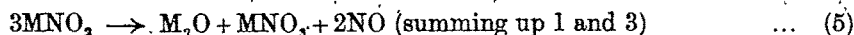
Thus, an exact determination of the amount of the alkali oxide in the residue at different stages in the decomposition can enable us to decide whether the nitrogen peroxide reacts in part also as in (4) or it reacts merely as in (3).

Four experiments were therefore performed on heating weighed quantities of pure $NaNO_2$ under different conditions at 380°, in a vacuum. Since glass is attacked by the alkali oxide, the nitrite was kept on a platinum surface. The platinum crucible, containing the substance, was enclosed in a glass tube heated in an electric furnace. The apparatus consisted of a glass tube passing through an internal seal to a flask containing some moist KOH and through the latter to the Sprengel pump. In the first experiment, a certain quantity of $NaNO_2$ was heated in a closed system till a certain quantity of gas was produced; in the second, the same quantity of $NaNO_2$ was mixed with its 25% $NaNO_3$ and heated in the same way: this was done to ascertain if the nitrate did decompose at this temperature and the results showed that it did; in the third, twice (that used in the first) the weight of pure $NaNO_2$ was heated under the same conditions as in the first with a view to finding the effect of mass and in the fourth experiment, the same weight (as that in the third) was heated with the pump working continuously so that the products of the reaction were not allowed to accumulate in the system and the surface reaction between the gas and the decomposing substance (also the solid products of the decomposition) was prevented. The results of these experiments are set out in Table IV.

TABLE IV

Experiments in the decomposition, at 380°, of $NaNO_2$ under different conditions

Wt. of substance (g.)	Time in hrs.	Total gas (c.c.)	Compn. of gas			Compn. of gas %		
			N_2O_3	NO	N_2	N_2O_3	NO	N_2
0.5000	55	14.82	0.4	5.7	8.7	2.7	38.4	58.8
0.5000+0.1250 NaNO$_3$	65	12.82	0.36	3.9	8.5	2.8	30.5	66.7
1.000	25	17.20	0.47	4.4	12.3	3.0	25.5	71.5
1.000	10	17.12	1.12	6.6	9.4	6.5	38.7	54.8

Residue in g.			Na_2O (Calc.)	Na_2O Ratio : Calc : Obs.	$NaNO_3$ formed per c.c. of N_2
NaNO$_3$	NaNO$_2$	Na$_2$O			
0.1085	0.3380	0.0331	0.0486	0.68	0.0124
0.2207	0.3612	0.0300	0.0416	0.72	0.0112
0.1500	0.7935	0.0450	0.0619	0.72	0.0121
0.1156	0.8210	0.0381	0.0537	0.71	0.0123

These results show that (i) a definite amount of nitrate is always produced per c.c. of nitrogen formed confirming the observation that nitrate and nitrogen-producing reactions go hand-in-hand; (ii) the oxide (Na_2O) actually found is less than what would be expected according to (5); (iii) the ratio, oxide (Na_2O) found to that formed according to (5), tends to remain constant during the reactions. This shows that all the nitrite used up does not decompose as in (1), but a *definite* fraction, indicated by the constancy of the ratio (iii), is used up as in (4). The above fact shows also that decomposition under study is a case of reactions proceeding in a homogeneous system. Hence, though the possibility of the

reactions (4) and (3) occurring at the gas-liquid (molten nitrite) interface is not precluded, the conditions prevailing in the system do not permit of escape of much nitrogen peroxide into the gas phase for reaction (4) to occur at the gas-liquid interface while the reaction (2), though it does occur at the interface, the extent of the reaction thus occurring must be very small since nitric oxide is much less reactive to nitrite than is nitrogen peroxide so that the ratio, nitrate : nitrogen, is not much affected by this heterogeneous reaction. In experiment 4, both nitrogen and nitric oxide are produced in amounts different from those in experiment 3 but it must be remembered that the effect of time is to produce more nitrogen (Oza and Shah, *loc. cit.*).

CONCLUSION

The mechanism of the reactions occurring in the thermal decomposition of sodium and potassium nitrites (presumably all alkali nitrites) may be represented as under :

I. The nitrites dissociate in the primary stage as

$$4MNO_2 \rightleftharpoons 2M_2O + 2NO + 2NO_2 \qquad \qquad \dots \quad (1)$$
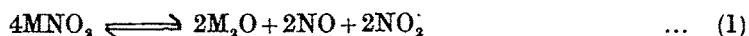
II. Nitrogen peroxide produced in (1) reacts with the oxide as in (2), and also with the undecomposed nitrite as in (3)

$$M_2O + 2NO_2 \longrightarrow MNO_2 + MNO_3 \qquad \qquad \dots \quad (2)$$

$$MNO_2 + NO_2 \longrightarrow MNO_3 + NO \qquad \qquad \dots \quad (3)$$
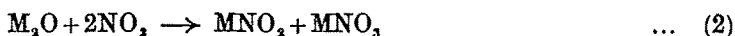
producing the nitrate.

III. The nitric oxide produced in (1) and (3) reacts with the unchanged nitrite to produce nitrogen as in (4)

$$2MNO_2 + 2NO \longrightarrow 2MNO_3 + N_2 \qquad \qquad \dots \quad (4)$$
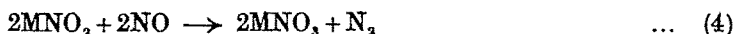
The reactions (2), (3) and (4) go hand-in-hand.

IV. All the reactions occur in the molten phase though the possibility of the reactions (2), (3) and (4) occurring at the gas-liquid interface, in a closed system, is not ruled out.

KARNATAK COLLEGE,
    DHARWAR.

CHEMICAL INVESTIGATION OF *SPILANTHES ACMELLA*

By V. G. Gokhale and B. V. Bhide

Flowers of *Spilanthes Acmella* have been chemically examined. The pungent principle has been shown to be identical with spilanthol which was first isolated by Gerber from *Spilanthes Olerdced*.

Spilanthol was isolated from *Spilanthes Olerecea* (N.O. *Compositœ*) or the American para cross by Gerber (*Arch. Pharm.*, 1903, **141**, 270). Spilanthol has been shown to be the *iso*butyl amide of decadienoic acid [Asano and Asahina, *J. Pharm. Soc.* (Japan), 1920, No. 460, 503 ; 1922, 85 ; Asano and Kanematsu, *Ber.*, 1932, **65B**, 1602].

The Indian variety, *Spilanthes Acmella*, does not appear to have been chemically examined. The flower head of *S. Acmella* has a hot burning taste and is a popular remedy for children who stammer. Recently we have found that the flower or the extract of the flowers is a powerful mosquito larvicide.

The flowers have been extracted successively with different solvents and it has been found that ether extracts the pungent principle effectively. The ether extract after removal of the solvent is treated with 60 % alcohol when an orange-coloured gum (A) separates. This gum does not possess the characterisitc pungent taste, nor does it give any crystalline substance. It is therefore hydrolysed by alcoholic potash and the unsaponifiable matter separated. The resulting semi-solid material is crystallised several times from alcohol and finally from ethyl acetate when a sterol, m.p. 184-85°, is obtained. Gerber (*loc. cit.*) has isolated a sterol, m.p. 178° from *Spilanthes Olerecea*. The mother-liquors give a white solid melting indefinitely between 75° and 81° but no homogeneous substance could be isolated.

On removal of alcohol from the extract a dark coloured liquid (B) is obtained from which spilanthol has been isolated.

The flowers do not give an essential oil in any appreciable quantity on steam distillation.

EXPERIMENTAL

The dry flower heads gave 8 % ash which consisted of potassium nitrate and small quantities of calcium and magnesium with traces of iron. Positive tests for phosphate, chloride and sulphate were also obtained. The flower heads did not give any test for alkaloids when extracted with Prolius fluid.

50 G. of the flowering heads were extracted successively with various solvents (Table I.)

The water extract did not reduce Fehling's solution but on boiling with dilute hydrochloric acid the solution readily reduced it thus showing the presence of polysaccharides.

3 Kg. of the flowering heads of the plant were extracted by cold percolation with ether. The ether extract was dried over magnesium sulphate and ether removed. The residue was a dark green viscous oil (35 g.). This extract was then extracted with 60%

TABLE I

Solvent.	% Wt. of extract.	Nature of extract.
Petrol (b.p. 40-60°)	0.57	Waxy material
Ether sulphuric	0.26	Dark green pungent liquid
Chloroform	0.05	Slightly pungent dark green liquid
Alcohol	0.8	„ „ „ „ „
Water	0.4	Sweet thick syrup

alcohol (80 c.c.) 3 times. The residue was an orange-coloured viscous mass (A) (15 g.) and had no pungent taste. The alcohol from the alcoholic extract was removed under reduced pressure and the residue was taken up in ether, the ether extract dried and ether removed. The residue (18 g.) (B) was a dark green oil and had pungent taste.

Examination of (A).—The substance was treated with a solution of potassium hydroxide (15 g.) in alcohol (50 c.c.) and benzene (10 c.c.) was added and the mixture was refluxed for 12 hours. The benzene and most of the alcohol were removed. The residue was suspended in a large quantity of water and repeatedly extracted with ether. The ether extract was dried and ether removed. The residue was a waxy yellow solid. It was crystallised several times from alcohol and finally from ethyl acetate when it melted at 184-85°. It gave all the colour reactions of a sterol. The mother-liquors on treatment with digitonin solution gave a further quantity of sterol on decomposition of the digitonide.

The alkaline solution on removal of the unsaponifiable matter gave a dark coloured liquid. This was crystallised several times from alcohol when a small quantity of an acid, m.p. 75-81°, was obtained but the quantity was too small for further investigation.

Examination of (B) : *Identification of Spilanthol.*—The alcohol extract (B) was taken up in ether, washed and dried over magnesium sulphate and ether was removed. The residue was distilled under 20 mm. pressure. The main fraction (10 g.) (C) distilled over at 220-225° as a pale yellow liquid leaving a black residue (5 g.) which could not be purified. The distillate (C) had a strong tingling taste when placed on the tongue. It contained nitrogen and absorbed bromine.

Maleic Anhydride Addition product of the liquid (C).—The liquid (5 g.) and maleic anhydride (5 g.) were dissolved in toluene (25 c.c.) and refluxed for 3 hours. Water (25 c.c.) was then added and the boiling was continued for another 1 hour. It was then cooled and the toluene layer was separated and washed with dilute sodium carbonate solution. The sodium salt of the adduct crystallised out. It was suspended in benzene and decomposed with dilute hydrochloric acid. The benzene layer was removed, washed with water, dried and benzene removed when a crystalline solid, m.p. 168-69° , was obtained. This is identical with the m.p. of the maleic anhydride adduct of the spilanthol isolated from *Spilanthes Olerecea* (Asano and Kanematsu, *loc. cit.*).

Oxidation of Spilanthol.—Spilanthol (5 g.) was dissolved in acetone (50 c.c.) and powdered potassium permanganate (30 g.) was added in small lots. A vigorous reaction

occurred and heat was developed.   On keeping overnight the acetone was recovered on a water-bath.   The residue was suspended in water and sulphur dioxide was passed in till all the manganese dioxide dissolved.   A small quantity of a white gum separated which was filtered off.   The filtrate was extracted with ether several times and the ether extract was dried and ether removed.   The residue on washing with a little benzene gave succinic acid, m.p. 184° (mixed m.p.).   Asano and Kanematsu (*loc. cit.*) obtained formic, succinic and butyric acids on ozonolysis of spilanthol.

A NOTE ON THE PHOTOCHEMICAL PREPARATION AND PROPERTIES OF TETRAIODOACETONE

By T. N. SRIVASTAVA

It has been pointed out in a previous communication (MacMahon and Srivastava, *J. Indian Chem. Soc.*, 1943, **20**, 311) that the reaction between sodium citrate and iodine (dissolved in KI) is negligibly slow both in light and dark at room temperature, but in the presence of certain catalysts such as Mn^{++} and Fe^{+++} the reaction proceeds rapidly in light with the production of a solid product. This solid compound has now been prepared in sufficient quantities by the following method.

Concentrated solution of sodium citrate was mixed with iodine solution in presence of small quantities of Mn^{++} and exposed to sunlight till the iodine was used up. The solid product formed was filtered off and the clear filtrate again exposed to sunlight after the addition of more iodine solution. The above operation was repeated until no further reaction with iodine took place. The yellow solid product, thus obtained, when recrystallised from warm benzene in the dark, melted at 142° with a previous change in colour. The molecular weight as determined by the cryoscopic method in the dark using benzene as solvent, and its percentage of iodine content, both correspond to the formula of tetraiodoacetone (CHI_2COCHI_2). This appears to be a convenient method for the preparation of the above compound and might be used as an alternative to the methods found in literature [Lederer, *Fortschritte der Theerfarbenfabrikation*, **5**, 710 ; Angeli and Levi, *Gazzetta*, 1893, **23**, 97].

At 22° the solubility of the compound in benzene is found to 3.4 g. per 100 g. of solvent, It is also soluble in toluene and to a lesser extent in chloroform, carbon tetrachloride and acetic acid. These solutions are extremely to sensitive and decompose photochemically producing free iodine and a solid resinous compound. In dark the solutions are fairly stable at room temperature (about 20°) but by raising the temperature to 40° decomposition takes place slowly.

CHEMICAL LABORATORY,
LUCKNOW UNIVERSITY, LUCKNOW.

OBITUARY

DR. SATYENDRA NATH CHAKRAVARTI

Born : 1903.
Died : August 28, 1945.

It is with profound sorrow that we record the news of the sad and premature death of Dr. S. N. Chakravarti, Chemical Examiner to the U. P. and C. P. Governments, under tragic circumstances.

Satyendra Nath Chakravarti was born in 1903 in Calcutta. After a brilliant career at the Lucknow University he went in 1926 for higher studies to Oxford and worked in the Dyson Perrins Laboratory under late Prof. W. H. Perkin, Jr., F.R.S. After taking the D.Phil. degree, he returned to India in 1929 and took up the appointment of Reader and Head of the Department of Chemistry in the newly established Annamalai University, South India. With his untiring zeal and love for research, he organised a flourishing school of chemistry. He devoted himself heart and soul to promoting success-fully its efficiency, by his continued and unselfish attention to its interests as a whole, not overlooking even the minutest administrative detail. The students owe much to his attention to the smooth running of the classes, as also to his constant interest in teaching fundamentals. The development of the courses for the Final Honours school fell to him—a task he accomplished with distinction. He was loved and respected by one and all in the University. He was a member of the Syndicate and Dean of the Faculty of Science. He became so popular that he was elected by the members of the Syndicate to act as Vice-Chancellor of the University for a period of 2 months. In the period from 1932-37 Dr. Chakravarti published several papers with his research students. Some of his work was inspired by that of Prof. W. H. Perkin, Jr. The subject investigated included—synthesis of isomers of tetrahydroberberine, a new method of synthesis of substituted phthalonic acids ; a synthesis of ψ-opianic acid ; synthesis of paraberine, hydroxy deriva-tives of naphthalene, investigation of Indian Medicinal Plants etc. His research students include Drs. K. Ganapati, P. R. Venkataraman, P. L. Narasimha Rao, Messrs. A. Venkatasubban, V. Pasupati, S. Aravamutachari, the present writer and a few others. Many of them are occupying important positions in different parts of India He was a member of the Council of the Indian Chemical Society for two terms.

It was to the great regret of his many pupils, colleagues and friends, that he left the academic life to take up the post of the Chemical Examiner to the U. P. and C. P. Govern-ments. Still many of his friends were hoping that he would come back to academic and research life, for which temperamentally he was admirably suited.

Dr. Chakravarti was a great and inspiring teacher. Quiet and modest in manner, unfailingly honest in his judgments and dealings with men, he proved a wise, independent,

courageous and respected counsellor to those who came in contact with him.   He had the capacity for carrying through administrative detail with great success ; in part this was due to his kind and generous nature, unfailing sense of honesty and his love for truth and justice.   Many of his students, colleagues and friends will recall with gratitude, the hospitality they received from Dr. and Mrs. Chakravarti in their home.   One of his few hobbies was bridge playing.

In his death India has lost one of her distinguished chemists and indeed one of her great and noble sons.

We offer our heartfelt sympathies to his berieved family.

<div align="right">M. SWAMINATHAN</div>

QUINOLINE DERIVATIVES. PART XI

By T. N. Ghosh and A. C. Roy

For pharmacological study against amoebiasis, 2-methyl-8-hydroxyquinoline-5-arsonic acid and 2-methylquinoline-6-arsonic acid have been synthesised.

The pronounced antiseptic property of chiniofon (sodium salt of 7-iodo-8-hydroxyquinoline-5-sulphonic acid) and of chinosol (8-hydroxyquinoline sulphate) is well known, the former drug being often used, with success, in the form of retention enema in chronic cases of amœbic dysentery. So far as the sulphonic acid group in chiniofon is concerned, it is difficult to arrive at the precise function of this group in relation to the pharmacological action of the compound. But the pronounced antiseptic property of chinnosol and vioform—compounds which are structurally allied to chiniofon but do not contain any sulphonic acid group—indicates that the function of the sulphonic acid group in chiniofon might be purely physical in that it confers solubility in aqueous medium to the sodium derivative of the compound.

The pronounced amoebicidal property of carbarsone or stovarsol indicates that it will be worth while to search for an ideal amoebicide in substituted phenylarsonic acid derivatives. In view of the above observations it has been considered to be of interest to synthesise 8-hydroxyquinoline-5-arsonic acid, the iodo derivative of which will be structurally related to chiniofon.

Some quinoline-arsonic acids are known in literature and they have been prepared by diazotising the corresponding aminoquinolines and treating the solution with sodium arsenite in the usual way. The arsonic acids are not obtained directly from the reaction mixture but are reduced to the arseno compounds, which are subsequently oxidised with hydrogen peroxide to yield the acids. This method is tedious and generally gives poor yields. It has been, therefore, considered desirable to explore other methods for the synthesis of quinoline-arsonic acids. Döbner and Miller (*Ber.*, 1881. 14, 2812) discovered that paraldehyde heated with aniline and concentrated hydrochloric acid gave quinaldine. The mechanism of this reaction was first satisfactorily explained by Beyer (*J. prakt. Chem.*, 1886, **33**, 423), who suggested that crotonaldehyde, produced from two molecules of paraldehyde, formed an additive product with aniline, ring-closure then proceeding as in the Skraup reaction (*cf.* Blaise and Maire, *Compt. rend.*, 1907, **144**, 93). Later work showed that this method of Döbner and Miller is of general applicability and that practically any aromatic amine may be condensed with an unsaturated aldehyde to give substituted quinolines.

Following the method of Döbner and Miller, 2-methyl-8-hydroxyquinoline-5-arsonic acid (I) has now been synthesised by the interaction of 3-amino-4-hydroxyphenylarsonic acid and paraldehyde. The compound (I) yields the

1

7-iodo derivative.   Similarly, by reacting *p*-arsanilic acid with paraldehyde under identical conditions, 2-methylquinoline-6-arsonic acid has now been obtained.
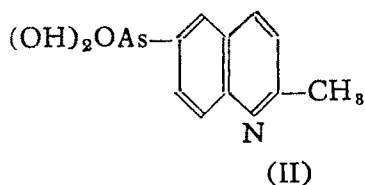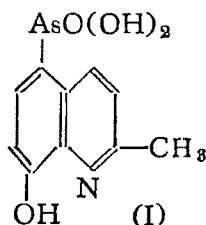
EXPERIMENTAL

2-Methyl-8-hydroxyquinoline-5-arsonic Acid (I).—3-Amino-2-hydroxyphenylarsonic acid (23 g.) was treated with commercial concentrated hydrochloric acid (19 c.c.). The hydrochloride, which was precipitated, was thoroughly triturated and to this mixture paraldehyde (freshly distilled, 14 c.c.) was added dropwise under shaking. Slight heat was generated and the hydrochloride gradually went into solution. The solution was allowed to stand for 1 hour and then heated under reflux in an oil-bath at 100-105° for 2 hours and then at 120-125° for 3 hours, and finally allowed to stand overnight.

Next day the solution was diluted with water, filtered and carefully neutralised, under cooling, with cold 10% sodium hydroxide solution, when a brown solid was precipitated. This was filtered, washed with water and then boiled with water 2-3 times till the filtrate became colourless. The solid is practically insoluble in almost all organic solvents and water, and was purified by dissolving in dilute hydrochloric acid and neutralising with cold 10% sodium hydroxide solution. The brownish solid was finally washed with hot alcohol and then with ether, yield 8 g. It is readily soluble in alkali carbonates and in mineral acids and does not melt even at 300°. (Found : As, 25.82 ; N, 4.49. $C_{10}H_{10}O_4NAs$ requires As, 26.50 ; N, 4.94 per cent). It does not contain any diazotisable amino group. A dilute hydrochloric acid solution of the compound gives immediately a brown precipitate with Mayer's reagent, a pale brown precipitate with potassium dichromate solution, and a pink colouration (gradually developed on standing) with ferric chloride solution.

7-Iodo-2-methyl-8-hydroxyquinoline-5-arsonic Acid.—A cold alcoholic solution of iodine monochloride (prepared from 2g. of iodine) was slowly added, under stirring, to a solution of the above compound (I, 4g.) dissolved in water (80 c.c.) containing sodium bicarbonate (1.2 g.). Immediately the iodo derivative was precipitated, which was allowed to stand for 1 hour with occasional shaking. It was filtered and washed thoroughly with water. It was next triturated with excess of 1% aqueous sodium bisulphite solution, filtered, washed with water, and then again tritutated with excess of 2% sodium thiosulphate solution, filtered and washed thoroughly with water and then with alcohol. The deep brown solid, thus obtained, is practically insoluble in almost all organic solvents and does not melt even at 300°. (Found : I, 30.28. $C_{10}H_9O_4NAsI$ requires I, 31.05

per cent). When heated with concentrated sulphuric acid, copious vapour of iodine is evolved. When a dilute nitric acid·solution of this compound is shaken with chloroform, the chloroform layer turns violet, the colour deepening on standing.

2-*Methylquinoline*-6-*arsonic Acid* (II).—Commercial concentrated hydrochloric acid (56 c.c.) was poured dropwise into a flask containing well powdered *p*-arsanilic acid (63g.), when the hydrochloride of *p*-arsanilic acid was formed. To this mixture was added dropwise paraldehyde (freshly distilled, 46 c.c.) under stirring, when there was slight rise in temperature and the hydrochloride gradually went into solution. The solution was then refluxed in an oil-bath for 3 hours at 120-25° and then allowed to stand overnight.

Next day the solution was diluted with water, and carefully neutralised under cooling, with cold 10% aqueous sodium hydroxide solution, when a brown solid was precipitated, which was filtered and washed thoroughly with water. It is practically insoluble in ·almost all organic solvents. It was triturated and washed with alcohol·and then with ether, yield 15g. The brownish solid does not melt even at 300° and is readily soluble in alkali carbonates and in mineral acids. (Found : N. 4.94 ; As, 28.61. $C_{10}H_{10}O_3NAs$ requires N, 5.24 ; As, 28.09 per cent).

The compound does not contain any diazotisable amino group. A dilute hydrochloric acid solution of the above compound gives a brown precipitate with Mayer's reagent, a pale brown precipitate with potassium dichromate solution and an insoluble zinc salt with a solution of zinc chloride in dilute hydrochloric acid.

STUDIES IN HYDROGEN BOND FORMATION.
PART II. ALCOHOLS

By. A. L Sundara Rao

In continuation of the work on amides, the association characteristics of methyl.and ethyl alcohols and phenol have been investigated. The changes in association are followed by the changes observed in the C – O frequency under different conditions of temperature and solution in polar and non-polar solvents The observed difference in the behaviour of the alcohols in solutions of water, as compared to that of the amides, has been explained as due to the difference in the types of polymers formed.

In continuation of the author's work on the molecular association of amides (*Science & Culture*, 1941, 6, 509 ; *J. Indian Chem. Soc.*, 1941, 18, 337) the association characteristics of the alcohols have been studied by the use of Raman effect, a short report of which has already appeared (*Science & Culture*, 1944, 9, 302). The alcohols chosen for study are methyl and ethyl alcohols and phenol.

In respect of physico-chemical properties, alcohols like water show highly abnormal properties. In Ramsay and Shield's equation for the surface tension of the liquids the value of K and X for methyl and ethyl alcohols are 0.93 and 3.4′ ; and 1.08 and 2.75 respectively as against 2.10 and 1.01 for normal liquids. The corresponding value for the association factor for phenol is 1.43. If these divergences are to be taken as an indication of the degree of molecular association, these liquids ought to be highly associated, particularly the methyl and ethyl alcohols.

The association in alcohols has been largely investigated in the infra-red region. These investigations have been concerned with the changes observed in the intensity and frequency of the absorption band of the hydroxyl group occurring at 3700 cm^{-1} (2.70μ) and 3400 cm^{-1} (2.94μ). The band at 2.70μ is ascribed to the C – H vibration of the isolated single molecules and that at 2.94μ to the associational O – H. Errera and Mollet (*Compt. rend.*, 1937. 204, 257) found that in very dilute solutions of aliphatic alcohols in CCl$_4$ and CS$_2$ the absorption band at 2.70 characteristic of single molecules is observed while the one at 2.9 tends to disappear. Increase of temperature is found to increase the intensity of the 2.70 band and to decrease that of 2.94. Observations on the absorption of the vapour support this view. Similar evidence for vapour like molecules of alcohol in CCl$_4$ solutions was reported by Kinsey and Ellis (*J. Chem. Phys.*, 1937, 5, 399), Freymann (*Compt. rend.*, 1937, 204, 41), Buswell and Rodebush (*J. Chem. Phys.*, 1937, 5, 501). On the other hand, Errera and Sack (*Trans. Faraday Soc.*, 1938, 34, 728) explained the association of alcohols in CCl$_4$ or CS$_2$ by the formation of double molecules and complexes of higher order, the latter vanishing rapidly with increase of temperature. The effect of solution of alcohols in oxygenated solvents like ether, acetone, nitrobenzene and

dioxane was studied by Gordy (*Phys.* *Rev.*, 1935, 50, 1161 ; *J. Amer. Chem. Soc.*, 1938, 60, 605), Freymann (*loc. cit.*), Badger and Bauer (*J. Chem. Phys.*, 1937. 5, 839), Errera and Sack (*loc. cit.*). The observed changes in the intensity and frequency of the vibration band of the C−H of the alcohol were explained as due to the formation of a weak inter-molecular hydrogen bond between the oxygenated compound and the alcohol.

The association in phenol like that of the alcohols has been mainly investigated in the infra-red region. Naherniac (*Compt. rend.*, 1932, 195, 1254) reported that phenol in the fused state has a wide absorption band with intensity maximum at 9853Å which shifts to 9776Å with increase of temperature. Brattain (*J. Chem. Phys.*, 1938, 6, 298) studied the effect of temperature on phenol and observed a small shift on the 3.1μ band from solid to liquid phenol which was further shifted at higher temperatures. From the small changes observed he concluded that the degree of association has not been appreciably changed. Evidence for the decrease of molecular association of phenol in solutions of carbon tetrachloride has been presented by Naherniac (*loc. cit.*), Freymann (*loc. cit*), Fox and Martin (*Nature*, 1937, 139, 507). The effect of solution of phenol in oxygenated solvents was studied in infra-red by Gordy and Nielsen (*J. Chem. Phys.*, 1938, 6, 12) who reported the formation of weak additive compounds by sharing the proton of the OH group. Huggins (*J. Org. Chem.*, 1936, 1, 407) cited evidence for the existence of weak additive compounds between phenols and ketones and between phenols and cyclic ethers which he attributed to hydrogen bridges.

From the Raman effect point of view the association in alcohols has been meagrely studied. Meyer (*Physikal. Z.*, 1931, 32, 293) reported that there is no difference between the spectrum of pure methyl or ethyl alcohol and that of a mixture of alcohol and CCl₄. Krishnamurty (*Indian J. Phys.*, 1931, 6, 401) reported that the only change that was observed in the spectrum of methyl alcohol in solutions of water is the shift of the C−O frequency at 1030 to lower values which he attributed to the formation of hydrates. Landsberg and Ukholin (*Compt. rend. U.S.S.R.*, 1937, 16, 391) studied methyl alcohol both in the liquid and the vapour state and found that the O−H band at 3400 shifts to 3680 which is ascribed to that of an unassociated O−H group. The association in phenol has not been studied at all. Only, the different investigators (*Monatas*, 1929, 52, 379ᵍ; *Indian J. Phys.*, 1929, 4,) 196 ; *Sci. Paper. Inst. Phys. Chem. Res. Tokyo*, 1929, 11, 205 ; *Z. physikal. Chem.* ; 1929, 48, 299) who worked with phenol contented themselves with a study of the pure substance at the laboratory temperature and a record is made of the number of Raman lines observed.

EXPERIMENTAL

It is evident from the foregoing summary, that not much work has been done from Raman effect point of view to understand the association characteristics of the alcohols. Hence, a systematic investigation of these was undertaken by the author. The alcohols were investigated at tem-

peratures of 5°, 30° and 60° (in the case of methyl alcohol) and 75° (in the case of ethyl alcohol). Phenol was investigated in the solid and liquid state and at 135°. The effect of solution in polar solvents like water, and non-polar solvents such as benzene and CCl_4 was studied. The effect of solution in an oxygenated solvent, acetone, was also investigated. Mixtures with ether could not be studied owing to the presence of an ether line 1028 close to the C—O line in the alcohols. Study of solutions of alcohol in nitrobenzene presents a similar difficulty. The method of purification of the liquids and the general experimental technique employed is described in detail elsewhere (*loc. cit.*).

Methyl Alcohol.

Raman Frequencies of Methyl alcohol.—This liquid has been studied by many investigators and there seems to be a general agreement between their results. The mean values of the various frequencies as given by Kohlrausch ("Der Smekal-Raman effekt" 1931, p. 309) are :

$$\Delta v = 1034 \ (5), \quad 1362 \ (0), \quad 1462 \ (5b),$$
$$2835 \ (6b), \quad 2943 \ (5b), \quad 3338 \ 85 \ Band.$$

Besides these, Ganesan and Venkataswaran (*loc. cit.*) have reported a line at 1257. It is probable that both the lines 1257 and 1362 are the C—H lines excited by 4078Å of the mercury arc. The Raman frequencies of methyl alcohol as measured by the author are as follows :

$$\Delta v = 1032 \ (6), \quad 1446 \ (4b), \quad 2832 \ (10b)$$
$$2928 \ (8b), \quad 2943 \ (5b), \quad 3378 \ (Band)$$

Of these the line at 1032 is well known to be due to the C—O oscillation ; 1446 corresponds to the CH_3 vibration. 2832 and 2928 are the valence C—H lines. The band at 3378 with a width of 430 cm^{-1} arises out of the O—H group in the alcohol.

Frequency Changes in Solution.—The changes observed in methyl alcohol lines due to solution in the various solvents are described below.

(*i*) *Non-polar*—Benzene and carbon tetrachloride have no effect either on the intensity or frequency of the Raman lines of methyl alcohol. This is in agreement with that reported by Meyer (*loc. cit.*).

(*ii*) *Polar and Normal*—Among the normal polar solvents used with advantage, is acetone. In mixtures of alcohol and acetone the 1032 line which is ascribed to C—O oscillation in methyl alcohol shifts perceptibly to the lower frequency.

(*iii*) *Polar and Abnormal*—Water, which belongs to this class of substances, brought about prominent changes in the C—O frequency, 1032, of methyl alcohol. Three concentrations were studied ; 100%, 75% and 25% by volume. The 1032 line is definitely shifted towards smaller frequencies (*cf.* Fig.

1 & 2). The shift is progressive, the maximum being in the lowest dilution where the 1032 line has shifted to 1010. The other lines remained more or less unaffected. It was not possible to study the effect of water on the O−H band of the alcohol due to the superposition of the water band on the alcohol O−H band.

Effect of Temperature.—Methyl alcohol was studied at 5°, 30°, and 70°. No prominent changes have been observed in the C−O line at 1032. The effect of increase in temperature on the O−H band, excited by the 3650 group of Hg lines, of methyl alcohol is perceptible (*cf.* Fig. 3). The intensity maximum of the band at 3378 cm⁻¹ at 5° shifts to 3438 cm⁻¹ at 30° and this is not further changed at 60°. The width of the band which is about 430 cm⁻¹ remains the same at all the temperatures investigated. The absence of any change in the intensity maximum of the band with increase of temperature from 30°−70° can be regarded as an evidence that the degree of association has not been appreciably changed. The shift of this band to lower frequencies in the spectrum taken at 5° indicates that it may be due to further association through hydrogen bonding.

Ethyl Alcohol

Raman Frequencies of Ethyl alcohol.—This liquid has been studied by many investigators, the most comprehensive one being that of Bolla (Z. *Physik*, 1934, 89, 513; 1934, 90, 607) who observed 56 frequencies of which 42 are combinational leaving 14 fundamental frequencies. There seems to be a fair agreement between the results reported by the various authors, and the mean values as given by Kohlrausch (*loc. cit.*) are :—

42 (1), 883 (5), 1046· (3),

1094 (1), 1273 (1), 1456 (4b),

2876 (5b), 2928 (7b), 2974 (5).

It is probable that the 1094 line owes its origin to 4046 excitation and is really the C−H line of frequency 2876. The Raman frequencies of ethyl alcohol as measured by the author are as follows :—

438 (1), 896 (6), 1052 (4),

1274 (2), 1455 (4b), 2874 (7b).

2929 (10b), 2958 (7), 3378 (Band).

In the case of the first member of the series of alcohols the assignment of the various frequencies to the different oscillations did not present much difficulty. But in the case of ethyl alcohol there seems to be a divergence of opinion between the assignments made to the different frequencies. This could be easily understood as the force constants of the C−OH and the C−C are very nearly the same, as the mass of the hydroxyl group differs from that of a methyl group by only two units.

Hibben ("The Raman Effect and its Chemical Application", p. 143) and the various other workers on the Raman spectrum of ethyl alcohol ascribe the 886 line to the C—O and the 1052 line to the C—C oscillations. The argument advanced in support of this is, that the C—C frequency in the corresponding hydrocarbon ethane is $\Delta \nu$, 993 and from the correspondence of this to the 1032 of methyl alcohol and as the frequency is generally supposed to decrease with increasing chain length, the 885 frequency occurring in ethyl alcohol has been ascribed to the C—O oscillation. But it is surprising, if the assignment is correct, why there should be such a marked shift of the C—O frequency of 1032 in methyl to 886 in ethyl alcohol. On the other hand, Venkataswaran and Bhagavantam (*Indian J. Phys.*, 1930, 5, 129), Canals and Gastaud (*Bull. soc. chim*, 1937, 4, 2042) on the basis of polarisation measurements, assign the partially polarised line near 1052 as due to the C—O. The changes observed by the author in solutions of water lend support to this assignment. It is difficult to conceive how the changes can be observed in the C—C oscillation (1052 according to the assignment of other workers) without at the same time noticing any changes whatsoever in the C—O oscillation (886 according to the assignment of other workers).

Hence, the author is inclined to think that the 886 is the C—C and the 1052 is the C—O frequencies in ethyl alcohol.

1455 is the δ (C—H) frequency and the three lines occurring at 2874, 2929, 2958 are due to the valence C—H oscillations. The O—H bond for ethyl alcohol occurs with an intensity maxium at 3378 cm^{-1}.

Frequency changes in Solution.—As far as the author is aware, this is the first systematic attempt to study ethyl alcohol in the various solvents. The changes observed in ethyl alcohol lines under the different conditions studied are described below :

(*i*) *Non-polar.*—Benzene and carbon tetrachloride have no effect either on the intensity or frequency of the Raman lines of ethyl alcohol.

(*ii*) *Polar and Normal.*—As in the case of methyl alcohol only mixtures of acetone and ethyl alcohol were investigated. The 1052 in ethyl alcohol shifts slightly to lower frequencies. No prominent changes have been observed in other lines. The complementary effect of ethyl alcohol on the acetone lines is more marked as observed by the frequency shifts of C—O of acetone.

(*iii*) *Polar and Abnormal.*—Water, which belongs to this class of substances brought about conspicuous changes. Three concentrations were studied—100, 75 and 25%. Taking the lines one after another their asssignments together with the changes observed are given below :

(*i*) $\Delta \nu = 886$ (C—C). No change is observed either in the intensity or frequency of this line.

(*ii*) $\Delta \nu = 1052$ (C—O), This line shifts to lower frequencies, the shift being 6 cm^{-1}.

(*iii*) $\Delta \nu = 1455$ (C—H). This line shifts appreciably to higher frequency.

1032

MeOH Pure

75%

25%

Fig. 1.

1032

70°C

CH₃OH Pure

25%
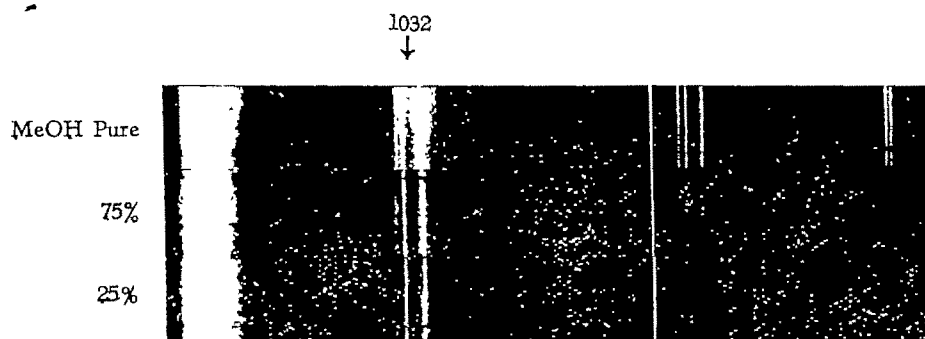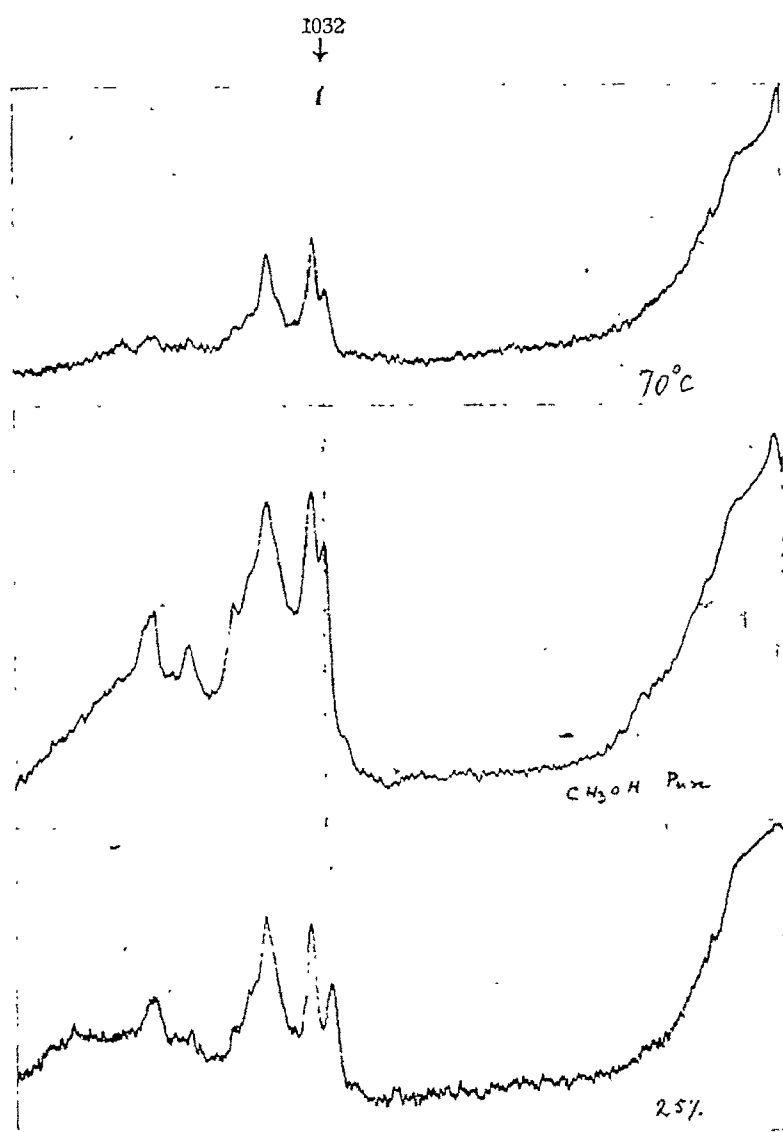
Fig. 2
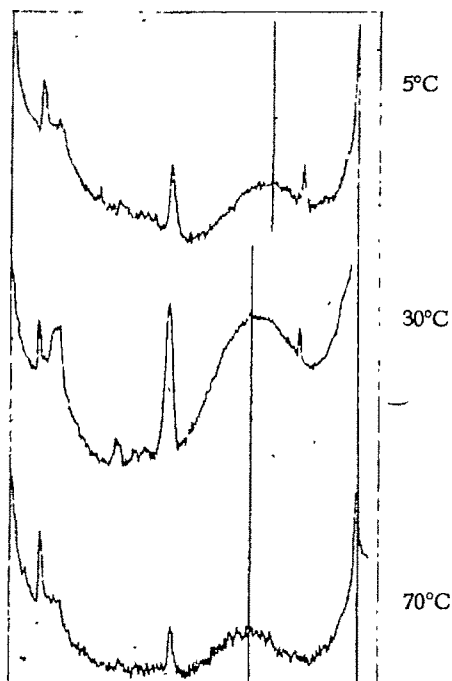
O – H *band of* MeOH *at diff. temp.*
Fig. 3.
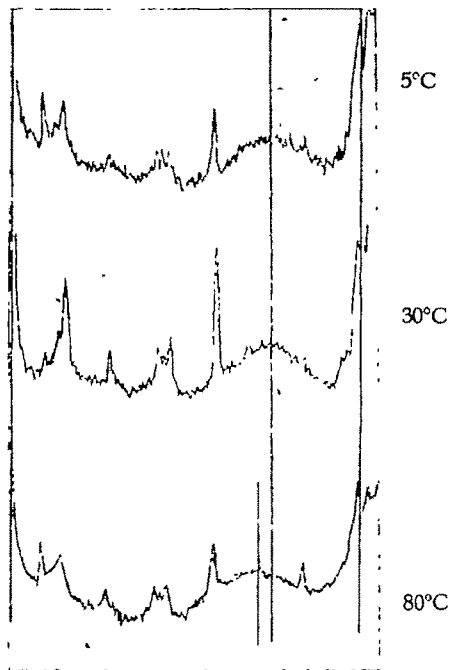
EtOH *at diff. temp.*
Fig. 5.
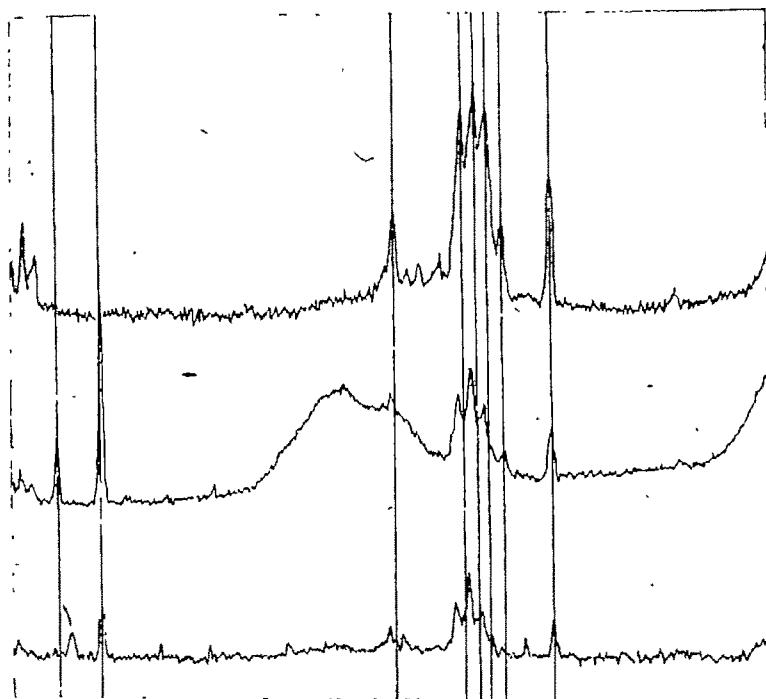
4916Å

C – H lines $\Delta \nu = 886$

EtOH – H$_2$O mixture
Fig. 4

(*iv*) $\triangle v = 1274$. This line becomes diffuse and broad and tends to disappear both on dilutions and at increased temperatures.

(*v*) $\triangle v = 2874, 2929, 2958$ (C—H). A very marked shift is observed in these lines (*cf.* Fig. 4.). With dilution there is a progressive shift of these lines towards higher Raman frequencies, the maximum shift observed in the lowest dilution is 30 cm⁻¹.

Effect of Temperature.—Ethyl alcohol was studied at 5°, 30°, and 80°. No prominent changes have been observed in any of the lines. The effect of increase of temperature on the O—H band in ethyl alcohol is perceptible. The intensity maximum of the band at 3378 cm⁻¹ at 30° shifts to 3403 cm⁻¹ at 75° (*cf.* Fig. 5). The width of the band, which is about 360 cm⁻¹, remains unaltered at all the temperatures investigated.

Phenol

Phenol was purified by repeated distillation under vacuum and the experimental technique employed is described in detail previously (*loc. cit.*). The Raman spectrum of the substance could be obtained in 10 hours by the author. The various Raman frequencies observed are given in Table I. Since some of the faint lines observed by the author have also been previously observed by Ganesan and Venkateswaram (*loc. cit*) but not included in the tabulated values as given by Kohlrasuch (*loc. cit.*), they are given in column I of Table I for purposes of comparison. Column II contains the values as given by Kohlrausch. In column III are given the Raman frequencies as measured by the author for solid and liquid phenol. Many new frequencies (noted with asteriks) have been observed.

TABLE I

Raman frequencies of phenol

I Ganesau & Venkateswaram.	II Kohlrausch	III Solid	IV Author Liquid
	235 (2)	246	230 (2)
	526 (2)	530	426* (1b)
616	614 (2)	620	530 (4)
763	758 (1)	760	620 (4)
818	813 (3b)	822	822 (7b)
			905* (1)
			940* (1)
1007	1002 (5)	1000	1000 (10)
	1024 (3)	1020	1025 (6)
			1065* (2)
1178	1170 (8)		1155 (5)
		1245	1245 (4b)
1363			1375 (1)
1495		1490	1495 (2)
1604	1598 (8)		1605 (5)
1360	8059 (5b)		8060 (10b)
3383			

The line at $\triangle v = 1000$ is the C—C frequency and the 1025 line is the C—O frequency. The line at 3060 is the valence C—H. Many of the other lines are those that arise from the benzene ring.

2

Frequency changes in Phenol at different Temperatures.

Solid-Liquid.—The frequency changes observed are as follows :—

(*i*) $\triangle \nu = 230$. This shifts slightly to lower frequency, the shift being 8 cm^{-1}.

(*ii*) $\triangle \nu = 822$. This line which is diffuse in solid is quite sharp in liquid.

Liquid, $\mathcal{C}0°-135°$. More perceptible changes were observed at higher temperature and the intensity and frequency changes of the various Raman lines are discussed below :

(*i*) $\triangle \nu - 760$. This is the feeble component accompanying the 822 line and tends to disappear at the higher temperature.

(*ii*) $\triangle \nu - 1025$. This diminishes considerably in intensity and shifts slightly to higher frequency with increase of temperature and the maximum shift observed at 135° is 5 cm^{-1}.

Frequency changes in Solution.—The changes observed in phenol lines due to solution in the various solvents are described below :—

Non-polar.—Carbon tetrachloride has no influence either on the intensity or frequency of the Raman lines of phenol.

Polar and Normal.—Among the normal polar solvents studied is acetone. In mixtures of acetone and phenol, the 1025 line. which is ascribed to the $C-O$ oscillations, shifts perceptibly to lower frequency. Besides this, one of the low frequency lines, $\triangle \nu = 620$, shifts slightly to lower frequency.

Polar and Abnormal.—Water is the prominent member which belongs to this class of substances. Unlike methyl and ethyl alcohols, which are miscible in all proportions, phenol froms with water what are called "Conjugate solutions" and it is only above the consolute temperature, which is 68.4°, that phenol and water are mutually soluble in all proportions and the system consists of but one liquid phase. Hence, solutions of phenol in water were studied at 80°. Great difficulty was experienced in the study of these solutions as they were getting coloured after a few hours' exposure to ultraviolet light and exhibited strong fluorescence. The only concentration which could be successfully studied was 10% by weight of phenol. The aqueous solution which exhibited strong fluorescence was purified by the method adopted previously in the case of sugars (*Indian J. Phys.,* 1940, 14, 207) and amides (*loc. cit.*) by treatment with carbon. A combination of two filters consisting of sodium·nitrite solution and iodine in carbon tetrachloride was used to photograph the Raman spectrum.

The following are the main changes that have been observed :

$\triangle \nu = 230, 530, 629, 760$. These are the low frequency lines which are probably due to intermolecular oscillations. All these lines are too feeble to be noticeable in solutions of water.

$\triangle \nu = 1025$ (C−O). No perceptible shift is observed in this line. The only changes that could be observed is the marked decrease in intensity, a change analogous to what has been observed with increase of temperature.

$\wedge \nu = 1245$. This line shifts to lower frequencies, the shift being 10 cm^{-1}.

D I S C U S S I O N

It has been suggested that the alcohols, phenols and water form associated chains as

$$
\begin{array}{ccccccc}
 & R & & R & & R & \\
 & | & & | & & | & \\
H\!\!-\!\!-O\!\!-\!\!-H\!\!-\!\!-O\!\!-\!\!-H\!\!-\!\!-O\!\!-\!\!-\text{etc.} &
\end{array}
$$
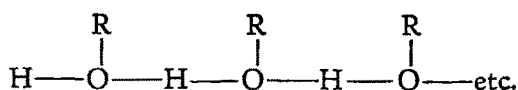
where the oxygen of the hydroxyl group acts as the donor and the hydrogen as the acceptor. Sidgwick ("Elecronic Theory of Valency", 1929, pp. 134, 149 ; *Chem. Rev.*, 1937, **20**, 259) suggested that this chain is not likely to contain more than 3 or 4 molecules. In the case of water, it is known with certainty[*] from both the X-ray and Raman effect data, that it is associated to triple molecules. In alcohols, the evidence (*J. Chem. Phys.*, 1934, **2**, 73) from the data on heats of mixing and the X-ray data of Zacharisen (*ibid.*, 1935, **3**, 158) point to the existence of double molecules. But there is other evidence from infra-red data, and the results obtained by Wulf (*Trans. Faraday Soc.*, 1937, **33**, 179) on the heats of dilution of alcohols, indicate the possibility of more complex grouping than double molecules. In solutions of water, which is of high dielectric constant, the tendency is to dissociate. This has been shown to be the case in amides by the author (*loc. cit.*). Koteswaram (*Z. Physik*, 1938 **110**, 118 ; 1939, **112**, 395) reported similar results in fatty acids. The conclusions arrived at in those substances were based on the changes observed in the $C-O$ frequency. Hence they are definite. It is only in the case of alcohols where there is only $C-O$ that it is found necessary to depend on the changes observed in this frequency.

In aqueous solutions of methyl alcohol, it was found that the $C-O$ line at 1032 shifts progressively to lower frequencies with increased dilution. This is an anomalous result with what has been observed in amides and acids. The difference in behaviour can be explained as follows. In the case of acids, which form closed ring complexes, the dimer structure has to be broken down first before any change can take place. It has been reported by Koteswaram (*loc. cit.*) that even at the largest dilutions there is no trace of evidence for the combination of water molecules with the acid molecules. In the case of alcohols, which form open chain compounds, a 'donor' and an 'acceptor' are both exposed at either end of the chain. Hence, the effect of solution in water may be that even without the breaking up of the polymer, the water can associate with the alcohol through the formation of a hydrogen bond. Hence, it is, that a shift of the 1032 line to the lower frequencies has been noticed. This is in agreement with the results obtained in infra-red by Gordy (*loc. cit.*) and by Krishnamurthy (*loc. cit.*) in Raman effect. A similar shift in the $C-O$ line of ethyl alcohol has also been noticed, though this is not as prominent as that observed in methyl alcohol.

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[*]There is an alternative hypothesis of the quasicrystalline structure of water first proposed by Bernal and Fowler (*J. Chem. Phys.* 1933, **1**, 515).

Meyer (*loc cit.*) reported that in solutions of methyl alcohol and water a line scarcely visible in the pure alcohol gets clearer as more water is added. It may be that this new line is nothing but the $C-O$ line. As Meyer has taken the spectrum of methyl alcohol with unfiltered mercury arc and probably with a small dispersion instrument, this line in pure alcohol might have been masked by the $C-H$ lines excited by the 4046 group of mercury lines which come very close to it. At larger dilutions in water, it shifts to lower frequencies and increases in intensity with increasing dilutions, and hence is more easily detected than the line in pure alcohol

Another very interesting change has been observed in the case of ethyl alcohol. The $C-H$ lines shift prominently towards the higher frequencies, while the $C-O$ line shifts to lower frequencies and no perceptible change is observed in the $C-C$ line.
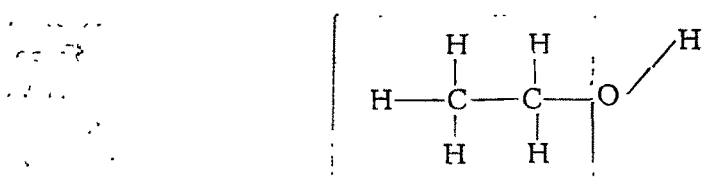
If the above were to represent the structure of ethyl alcohol, in solutions of water the $C-O$ bond weakens due to association with water molecules and consequently the rest of the molecule, enclosed by the dotted line, gets strenthened. Hence it is, that a change towards higher frequencies of the $C-H$ lines is noticed. It is surprising that no similar change is observed in the $C-C$ binding. Besides these changes, the deformation frequencies undergo prominent shifts.

The change of temperature from 5° to 70°C brought no changes in the $C-O$ line or any of the other lines thereby showing, that in the temperature range investigated, the degree of association has not appreciably changed. The effect of temperature on the $O-H$ bands in the alcohols is perceptible. Similar conclusions ware arrived at by Badger and Bauer (*loe. cit.*) who report the absence of a sharp $O-H$ band in methyl alcohol even at 71°. But they, however, report that it is quite evident in ethyl alcohol.

The line $\Delta\nu = 822$, which is diffuse in solid phenol, is sharp in liquid phenol which indicates depolymerisation. The feeble component 760 of the 822 line disappears at the higher temperature. It is likely that the 760 line might be due to the polymers which are present at the laboratory temperature. The slight shift of the 1025 line to higher frequencies from solid phenol to liquid phenol at 135° indicates that the degree of association has not been very much changed. Besides these, the deformation frequency occurring at 1405 undergoes a shift to the higher frequency. The changes observed in solutions of water seem to indicate depolymerisation. The low frequency lines which are characteristic of the intermolecular oscillations disappear in solutions of water thereby showing that water, which is a high dielectric, decreases the polymerisation of

phenol and hence the lines, which are characteristic of associated groups, disappear. This observation is dissimilar to what has been noted in the aliphatic alcohols, but is in aggreement with the general phenomenon occurring in other associated substances (e.g., acids, amides.)

Besides this, the 620 line shifts to lower frequency. It has been previously shown by Koteswaram (*loc. cit.*) in acetic acid and by the authot (*Indian J. Phys.*, 1929, **14**, 365) in glycerine that this line is susceptible to changes in association.

The slight shift to the lower frequencies of the C−O line in the alcohols and in phenol in solutions of atetone, indicates that a weak intermolecular hydrogen bond had been formed between the hydroxyl group of the alcohol and the keto oxygen, as

$$\begin{array}{c} R \\ \diagdown \\ \diagup C = O \longrightarrow H - O \diagup^{R \text{ or } R'} \\ R \end{array}$$
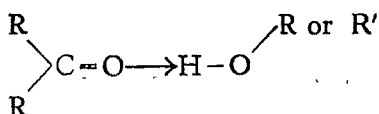
In conclusion the author desires to express his grateful thanks to Dr. I. R. Rao, under whose guidance the work was done.

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EFFECT OF AGEING ON THE CONDUCTIVITY OF SOLS

By S. D. Jha and S. Ghosh

In this paper the changes in electrical conductivity of the sols of stannic hydroxide, ferric phosphate and vanadium pentoxide on ageing have been investigated. The nature of the changes taking place in this property, depends upon the behaviour of colloidal particles and concentration of the sol. The changes have been more prominent in the case of most dilute sols. In general the adsorption capacity of the particles decreases on ageing, resulting in an increase in electrical conductivity except in some cases where some of the substances present in solution, polymerises to give some complex aggregates, causing a decrease in conductivity.

It is well known that the physical properties of colloids considerably change on ageing. Gessner (*Koll—chem. Beih.*, 1924, **19**, 213,) studied the properties of vanadium pentoxide sol in detail and noted a decrease in conductivity with time. Rocasolano ("Colloid Chemistry" by J. Alexander, Vol. II, p. 99) found that the electrical conductivity of colloids vary within wide limits; an increase in the care of silver sol and a decrease in the case of calf-serum was noted by him. Dhar and Chakarvarti (*Kolloid Z.*, 1927, **42**, 120 ; *Z. anorg. Chem.* 1927, **168**, 209) have reported the effect of ageing on the electrical conductivity of sols and concluded that in general lyophobic sols show an increase while lyophilic ones show a decrease in electrical conductivity. Lottermoser and Lesche (*Koll.-chem. Beih.*, 1931, **32**, 157) have observed that the electrical conductivity of ferric hydroxide sol, which is usually regarded as lyophobic sol, increases on ageing. Similarly Desai and co-workers (*Trans. Nat. Inst. Sci. India*, 1939, **2**, ii, 39) report that in general the sols of arsenious sulphides, gold and vanadium pentoxide decrease in their electric charges on ageing as obtained from cataphoretic speed measurements. These sols also become unstable to some of the coagulating electrolytes and the specific conductivity generally decreases on ageing of the sols. In this paper we have studied the effect of ageing on the conductivity of some sols of different purities and concentrations.

Experimental

For conductivity measurements Rowland's bridge was used. In place of the induction coil, an electrically operated tuning fork of low frequency was used. The conductivity cell was well-platinised so as to give sharp minimum points. The conductivity was found at 30° by placing the cell in a thermostat in which the temperature could be easily adjusted to within $\pm$ 0.1°. The bridge was calibrated for the cell constant using the modified method of Wark (*J. Phys. Chem.*, 1930, **34**, 885). Graph for the cell constant and different readings of the bridge was plotted and the value of cell constant corresponding to any bridge reading was obtained from the graph. A higher order of accuracy may be obtained by employing this method as illustrated below. Results obtained by taking the mean cell constant are also given for comparison.

TABLE I

N/10-KCl solution. Temp. = 30°.

Resistance in ohms.	Bridge reading.	Cell constant.	Sp. condy. with mean cell const.	Sp. condy. from graph.
2	86·5	0·1871	0·01520	0·01481
8	81·3	0·1914	0·01483	0·01456
4	76·85	0·1938	0·01468	0·01459
5	72·5	0·1924	0·01478	0·01459
10	57·35	0·1966	0·01446	0·01459
15	47·55	0·1985	0·01433	0·01459
17	44·3	0·1972	0·01443	0·01460
20	40·3	0·1971	0·01448	0·01460
25	86·1	0·1973	0·01441	0·01459
27	33·45	0·1981	0·01436	0·01460
30	31	0·2032	0·01400	0·01459
35	27·95	0·1985	0·01505	0·01459
40	25·35	0·1982	0·01435	0·01459

It is evident from the above, that the error is very much reduced by using this method, and the results are practically constant.

Stannic Hydroxide Sol

The sol was prepared as mentioned in a previous paper (*J. Indian Chem. Soc.*, 1945, 22, 23). The various samples of sol at different stages of purity (A, A′, A″, A‴) were taken out and diluted to their one-third and one-ninth concentration and stocked in the same way. The results of specific conductivity as measured at 30° are given below.

TABLE II

Conc. of sol A = 45.16 g/l.
Conc. of $(NH_4)^+$ = 1.36 g/l.

No. of days.	Sp. condy × 10⁵ mho		
	Sol A.	Sol A/3.	Sol A/9.
0	2·350	0·819	0·806
7	2·288	0·903	0·870
20	2·220	0·910	0·439
45	2·169	0·9202	0·480
61	2·211	0·9896	0·5496
103	2·255	0·9913	0·6101

TABLE III

Conc. of sol A = 42.40 g/l.
Conc. of $(NH_4)^+$ = 0.823 g/l.

No. of days.	Sp. condy. × 10³ mho		
	Sol A′.	Sol A′/3.	Sol A′/9.
0	1·340	0·431	0·1824
6	1·300	0·559	0·2130
19	1·257	0·5780	0·2350
44	1·140	0·5459	0·2299
59	1·187	0·5720	0·2444
102	1·290	0·6235	0·2945

TABLE IV

Conc. of sol A″ = 36.58 g/l.

Conc. of $(NH_4)^+$ = 0.501 g/l.

Sp. condy × 10⁻³ mho

No. of days.	Sol A″.	Sol A″/3.	Sol A″/9.
0	0 887	0·2996	0·113
14	0·789	0·8660	0·1581
21	0·788	0 4550	0·1780
43	0·7541	0·3542	0 1847
57	0 7877	0·3681	0·1904
99	0·8184	0·3890	0·2036

TABLE V

Conc. of the Sol A‴ = 32.92 g/l.

Conc. of $(NH_4)^+$ = 0.295 g/l.

Sp. condy. x10⁻³ mho

No. of days.	Sol A‴.	Sol A‴/3.	Sol. A‴/9.
0	0 5740	0·224	0·0978
10	0·5725	0·255	0·1140
21	0 5300	0·256	0·1180
42	0·5146	0·262	0·1239
52	0·5337	0·2679	0·1263
90	0·5400	0·2720	0·1304

TABLE VI

Conc. of sol B = 51·52 g/l.

Conc. of Cl ion = 0·236 g. ion/l.

Sp. condy, × 10⁵ mho

No. of days.	Sol B.	Sol B/3.	Sol B/9.
0	32·61	15·63	6·80
12	33·40	16·36	7·72
33	32·28	16·01	6·86
50	32·16	15·55	6·404
65	32·49	15·43	6·899

TABLE VII

Conc. of sol B′ = 37·30 g/l.

Conc. of Cl ion = 0·096 g. ion/l.

Sp. condy. × 10³ in mho

No. of days.	Sol B′.	Sol B/3.	Sol B/9.
0	12·55	5·95	2·72
10	13·12	6·372	2·83
21	13·02	6·201	2·805
41	12·65	6·194	2·766
50	13 89	6·186	2·804

TABLE VIII

Conc. of sol B″ = 24.67 g/l

Conc. of Cl ion = 0.0047 g. ion/l.

Sp. condy. x10⁵ mho

No. of days	Sol B″	Sol. B″/3	Sol B″/9
0	2·62	1·478	0·742
7	3·030	1·679	0·836
28	2·565	1·763	0·862
45	2·409	1·775	0·889
61	2·789	1·736	0 8904

TABLE IX

Conc. of sol B‴ = 31.63 g/l

Conc. of Cl ion = 0.0022 g. ion/l.

Sp. condy. x10⁺⁴ mho

No. of days	Sol B‴	Sol B‴/3	Sol B‴/9
0	1·962	1·086	0·5405
5	2·078	1·172	0·5984
26	2·187	1·234	0·6360
49	2·160	1·233	0·6256
58	2·231	1·244	0·6298

Vanadium Pentoxide Sol and Ferric Phosphate Sol.

The sols were prepared as reported in a previous paper (*loc. cit.*) and samples were taken out at different stages of purity and designated as B, B′, B″ (ferric phosphate) and C, C′, C″ and C‴ (V_2O_5 sol). The conductivity measurements were done at 30°.

TABLE X

Conc. of sol C = 12.012 g /l.

Sp. condy. $\times 10^4$ mho

Time.	Sol. C.	Sol C/3.	Sol C/9.
0 days	3·803	3·127	2·173
12	3·467	3·193	2·660
26	3·228	3·063	2·450
52	3·208	2·909	2·337
70	3·166	2·826	2·290
88	3·125	2 643	2 013

TABLE XI

Conc. of sol C′ = 11.466 g./l.

Sp. condy. $\times 10^4$ mho

Time.	Sol C′.	Sol C′/3.	Sol C′/9.
0 days	3·548	2 996	2·140
10	3·420	3·009	2·321
24	3·374	3·692	1 957
50	3·042	2 507	1·858
68	3·003	2·415	1·854
86	2·963	2·388	1·825

TABLE XII

Conc. of sol C″ = 10.556 g./l.

Sp. condy. $\times 10^4$ mho

Time.	Sol C″.	Sol C″/3.	Sol C″/9.
0 days	3·390	2·489	1·606
8	3·345	2·950	2·098
22	3·155	2·815	2·053
47	3·012	2 757	1·966
65	2·887	2·671	1·939
88	2·717	2·601	1·893

TABLE XIII

Conc. of sol C‴ = 9.828 g./l.

Sp. condy. $\times 10^4$ mho

Time.	Sol C‴.	Sol C‴/3.	Sol C‴/9.
0 days	3·210	2 144	1·864
6	3 144	2·787	1 966
22	3·012	2·763	1·743
47	2·867	2·757	1 656
65	2 719	2·368	1·643
82	2·638	2·124	1 641

DISCUSSION

The results on the changes in electrical conductivity show that the nature of the change is different not only for the different sols, but in the case of stannic hydroxide sol it differs with the concentration of the sol investigated. An increase in conductivity in the case of diluted sols of stannic hydroxide and ferric phosphate has been noted, while there is a decrease in the concentrated sols of stannic hydroxide and vanadium pentoxide. A sol of vanadium pentoxide contains sufficient vanadic acid in solution which polymerises on ageing, and that the vanadate ions are preferentially adsorbed on the colloidal particles. This means that a sol of vanadium pentoxide would contain smaller amounts of substances in the dissolved condition when it is allowed to age, with

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the consequent decrease in the electrical conductivity. In the case of dilute sols of vanadium pentoxide an increase in electrical conductivity followed by a decrease has been noted, and it appears that when a sol of vanadium pentoxide is diluted, due to the increase of the water content of the sol, more of vanadic acid ions slowly come into solution. These finally aggregate again to form polymerised molecules or colloidal particles, producing the changes in electrical conductivity as noted.

A sol of stannic hydroxide, peptised by ammonia, is a complex aggregate of ammonium stannate and we are of opinion that a sol of stannic hydroxide resembles a sol of vanadium pentoxide in this respect. Ammonium stannate in solution, on ageing undergoes hydrolysis in solution, forming colloidal stannic hydroxide. Such a chemical change in solution would necessarily result in a decrease in electrical conductivity of a stannic hydroxide sol. The decrease in conductivity of the concentrated sol of stannic hydroxide, has been noted up to a certain minimum, after which there is an increase. As it is natural tendency of all colloidal particles to give out adsorbed electrolytes with age, this explains the increase noted in the later part of the observations. In the case of dilute sols the hydrolysis is very nearly complete, and the equilibrium between adsorbted and free electrolytic ions is gradually shifted due to an excess of water being present. That is why, there is a continuous increase in the electrical conductivity of the dilute sols of stannic hydroxide, the phenomenon being most prominent with very dilute sols. In the case of ferric phosphate sols, there is in general an increase in the electrical conductivity of the sols, the changes being more prominent for the dilute sols than for the concentrated ones. In the case of concentrated sols of ferric phosphate, there has been a tendency towards increase in the electrical conductivity, although these values are not very regular because of the growth of moulds of phosphate with age.

In general, with regard to changes in electrical conductivity of sols on ageing, it may be expected that the adsorbed electrolyte on the colloidal particles shall come out, due to a decrease in the adsorbing capacity of the colloidal particles with time, resulting in an increase in the electrical conductivity of the sols on ageing. This is confirmed by our results that the dilute sols show more marked changes in conductivity. In the case of such sols, as vanadium pentoxide however, there is a decrease in the electrical conductivity, because the dissolved vanadic acid polymerises with age.

FIXED OIL FROM THE SEEDS OF *ARTOCARPUS HIRSUTA*, LAMK

By N. S. Varier

The oil from the seeds of *Artocarpus Hirsuta* has been chemically examined and the component acids isolated.

Artocarpus Hirsuta (Malayalam-*Anjili*) is a tree found in the evergreen forests of the west coast. The oil expressed from the seeds is used locally, in medicine and as an edible oil.

The seeds used in this work were obtained from North Travancore, each air-dried seed weighs about 0·3g. It consists of a white thin outer skin (9·6% by weight on air-dried seeds) and a kernel (90·4%) with a bitter taste. The air-dried kernel contains 17·8% moisture and 7·9% ash. The ash contains carbonate, chloride, phosphate, iron and potassium.

EXPERIMENTAL

18.26 G. of the air-dried powdered seeds were extracted successively in Soxlet with different solvents. The results are given in Table I.

TABLE I

Order of extraction.	Name of solvent.	Weight	Percentage extracted.	Nature of extract
1.	Petrol (50 – 60°)	3 5 g.	16·17	Oil.
2.	Chloroform	0·32	1·75	Green waxy solid
3.	Ether	0·03	0 16	Thick pasty mass
4.	Ethyl acetate	0 12	0·64	
5.	Alcohol	4·10	22·45	Resinous powder.
		8·07	44·17	

The oil, obtained by extraction with petrol, had the following constants : Specific gravity at 30°=0.92 ; Ref. Index (30°)−1.4762 ; Acid value=4·0 ; Saponification value=179.0 ; Iodine value = 85.05 ; Hehner value=91.00% ; Richert Meissel value=Nil ; unsaponifiable matter=1.3%

The fatty acids liberated from the oil after hydrolysis in the usual manner (Mean molecular weight, 306.9 ; Iodine value, 99.66) were resolved into solid (31.8%) and liquid (68·2%) acids by the lead-salt alcohol method.

A. The Liquid Acids.

Iodine value (Winkler) =113.1 ; mean molecular weight, 279.4. They were dissolved in ether, cooled in ice and treated, drop by drop, with bromine in glacial acetic acid (1 c. c. in 3 c.c.) till the colour of bromine was permanent. No hexabromide separated even after 24 hours. The liquid was washed with thiosulphate solution, dried, and the ether driven off. The residue was dissolved in hot petrol (50°-60°). On cooling in ice, a brown powder separated which

melted at 114° after recrystallisation from petrol and did not depress the melting point of linoleic tetrabromide.

From the filtrate the petrol was driven off when a liquid bromide resulted. This may be oleic dibromide.

Oxidation of the Liquid Acids.—The acids (2 g.) were dissolved in dilute alkali and the resulting soap was dissolved in 400 c. c. of water. To this 1.5% solution of potassium permanganate was . added. It was left for 10 minutes and the excess of permanganate was destroyed by passing sulphur dioxide, when a white suspension of oxidised acids resulted. This was filtered and washed many times with water and then with a little ether. This residue was extracted with a large quantity of ether. The ether extract, after concen-tration, yielded a crystalline acid, m. p. 126°-28°. After recrystallisation this melted at 130°-31° and did not depress the melting point of dihydroxystearic acid. The ether-insoluble part was extracted with hot water. The hot water extract on cooling gave an acid, m. p. 162°—63°. After recrystallisation this melted at 163°-64°. Molecular weight = 345.8 (tetrahydroxystearic acid Mol. wt. 348).

From the molecular weight and the m. p. it would appear that the solid is one of the tetrahydroxystearic acids.

B. The Solid Acids.

These were obtained as colourless solid with a waxy appearance, m. p. 78°-79°.

Fractional Precipitation by lead acetate.—About 5 g. of the acids were dissolved in 100 c. c. of hot alcohol and 3 c.c. of hot 10% alcoholic solution of lead acetate were added successively 5 times. The lead salt liberated in each case was decomposed by dilute nitric acid and the acids were dissolved in ether and washed and dried The m. p. and mean molecular weights were determined in each case.

TABLE II

Fractions.	Weight.	M.p.	Mean M. W.
A₁	1·0 g	80°	377·8
A₂	0·5	80°	366 8
A₃	1·3	80°	368 0
A₄	1·0	74°	
A₅	1·0	35 – 38°	

Fractions A₁, A₂ and A₃ were mixed together and recrystallised many times from alcohol yielding finally an acid, m. p. 82° (mean M. W., 392.3).

This was suspected to be cerotic acid (m p. 78-82°, molecular weight 396) This has been confirmed by the preparation of the ethyl and methyl esters of the acid in the usual manner and by determining the molecular weight by the silver salt method. Ethyl ester, m. p. 56°, after recrystallisation from acetone m. p. 58°-59°; ethyl cerotate melts at 59° (Lewkowitch).

The acid was regenerated from the ester by boiling with alcoholic potash, m. p. 81° (mixed m. p. with original acid, 81°).

The ester distilled without decomposition under reduced pressure.

Methyl ester.—M. p. 60°; after recrystallisation from acetone, m. p. 60-61°; methyl cerotate melts at 60° (Lewkowitch). [Found (silver salt): Ag, 21.32, 21.46. $C_{26}H_{51}O_2Ag$ requires Ag, 21.47 per cent].

Fractions A_4 and A_5 were mixed together and again separated into solid and liquid acids, dissolved in alcohol and water added gradually to the solution to reprecipitate the acids. Three fractions were thus obtained.

TABLE III

Fractions.	M.p.	Mean M W.
B_1	78°	356·0
B_2	57°	268·9
B_3	59°	259·8

Fraction B_3 was recrystallised thrice from alcohol, m. p. 61° (mixed m. p. with pure palmitic acid, 61-62°).

Methyl esters of the Solid Acids.—The solid acids, prepared from a fresh quantity of the oil, were converted into methyl esters in the usual manner with 3% methyl alcoholic hydrochloric acid. After drying in vacuum, 15 g. of the esters were distilled under reduced pressure (3−5 mm.) and six fractions were obtained. All these fractions were saponified separately, the corresponding acids were liberated and these were crystallised to isolate the acids.

TABLE IV

Fractions.	B. p./3-5 mm.	Weight.	Mean M. M.	M.p. of acid.
S_1	150-160° (boils mostly at 155°)	0·8 g.	268	60°
S_2	170-180° (mostly at 176°)	1·05	304	66°
S_3	180-200° (mostly at 196°)	3·50	350	74°
S_4	200-215° (mostly at 210°)	3·1	377 6	80°
S_5	215-230° (mostly at 225°)	3·1	390·0	82°
S_6	230-240° (mostly at 235°)	3	392·0	82°

Unsaponifiable matter.—This was obtained as a waxy, brownish yellow mass. It gave the usual colour reactions for phytosterols.

STUDIES ON THE DICHROISM OF VANADYAL COMPOUNDS
PART I. MEASUREMENT OF ROTATORY DISPERISION AND
AND CIRCULAR DICHROISM OF- AMMONIUM
VANADYL TARTRATES

By B. C. Kar.

The rotatry dispersion and circular dichroism ˉof· ammonium vanadyl tartrates have been studied.

In a previous publication (Ghosh, *J. Indian Chem. Soc.*, 1939, **16**, 57) it has been shown that a photocatalytic dichroic system for visible radiations can be obtained by reducing in ordinary light a mixture of sodium vanadate and excess of *d*-tartaric acid. The circular dichroism and optical activity are due to the fact that a violet coloured solution is obtained when the pentavalent vanadium (V^5) is reduced to the quadrivalent stage (V^4) by excess of tartaric acid. But the exact nature of the complex formed between vanadium and tartaric acid was not studied. In this communication the actual complex has been isolated and some of its properties including rotatory dispersion and circular dichroism have also been studied.

Preparation of Ammonium Vanadyl Tartrates.—The salt was prepared by the method of Rosenheim and Mong (*Z. anorg. Chem.*, 1945, **148**, 31). Ammonium metavanadate $(NH_4)VO_3$ (10g.) was suspended in water and boiled with hydrobromic acid when a deep blue solution was obtained. The solution was then evaporated to a small volume and 12 g. of *d*-tartatic acid were added. To prepare the ammonium salt, the solution was then treated with strong ammonia until it was neutralised. The solution became violet showing the formation of the complex. On cooling it in ice-cold water, fine crystals were separated. It was then filtered and washed thoroughly with ice-cold water and dried over calcium chloride in an atmosphere of carbon dioxide in a vacuum desiccator. To obtain the pure product it was recrystallised several times from distilled water and preserved in an atmosphere of carbon dioxide. The molecular formula of the complex as given by Rosenheim is

$$\left[\begin{array}{l} COO\diagdown \\ CHO- \\ CHO- \\ COO\diagup \end{array} \left(VO \right) \right] R_2$$
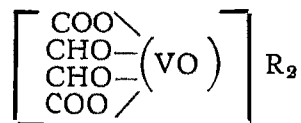
where R = (NH_4), Na, K, etc.

Measurement of Circular Dichroism.—Circular dichroism was measured by means of the·· Bruhat's apparatus which has an observational error $\pm 0 \cdot 02°$ (*Bull. soc. chem.*, 1930, **47**, 251). Extinction coefficient was determined by means of König-Martens spectrophotometer inˉan air-tight small rectangular cell of 5 mm. thickness The solution of the substance of known strength was made in distilled water and preserved˴in a Thunberg tube, the last traces of oxygen being removed by washing the tube·with carbon dioxide several times. The measurement of˴circular dichroism was carried out in a Baly's tube The end plates of the tube was entirely freeˉfrom ellipticities. The light source was a point-o'lite lamp of 1000 c.p. and monochromatic radiations were obtained by

passing the light through a monochromator. The circular dichroism has been expressed as anisotropy factor g, where $g = \dfrac{\epsilon_l - \epsilon_r}{\epsilon}$ in which ϵ_l, ϵ_r and ϵ are the molecular extinction coefficients for the left circularly polarised light, right circularly polarised light and ordinary plane polarised light respectively.

$$\text{Now } \epsilon_l - \epsilon_r = \frac{4\phi}{cl} \log_{10} e \text{ and } \epsilon = \frac{2(\log \tan \theta_2 - \log \tan \theta_1)}{cl}$$

where ϕ is the ellipticity expressed in radians, c is the molecular concentration, l is the length of the column of solution ; θ_1, and θ_2 are the spectrophotometer readings.

If e is expressed in degrees we have

$$g = \frac{4 \times 22 \times 0.4343\phi}{7 \times 180 \times c \times l} \times \frac{c \times l}{2(\log \tan \theta_2 - \log \tan \theta_1)}$$

$$= \frac{4 \times 22 \times 0.4343 \times \phi}{7 \times 180 \times 2 \,(\log \tan \theta_2 - \log \tan \theta_1)}$$

The results of the rotatory dispersion and circular dichroism are given below.

TABLE I

Conc. of Am. vanadate $= M/10$

$p_H = 4.2$. Temp $= 28.9°$. $l = 5$ mm.

λ	Rotation	Ellipticity	$(\log \tan \theta_2 - \log \tan \theta_1)$ $(l=5\text{mm.})$	g.
6500 Å	+1·05	−1·13	0·4082	−0·04199
6438	+1·11	−1·40	0·4313	−0·04922
6200	+1·79	−1·47	0·4486	−0·05025
6000	+2·48	−1·15	0·3936	−0·04431
5900	+3·00	−0·62	0·3413	−0·02755
5780	+3·22	−0·17	0·2928	−0·008804
5660	+3·52	+0·88	0·3118	+0·01848
5560	+3·52	+1·22	0·4158	+0·04451
5500	+3·40	+1·27	0·4158	+0·04634
5461	+3·28	+1·58	0·4630	+0·05176
5360	+2·76	+2·22	0·5719	+0·05754
5300	+2·10	+2·47	0·6032	+0·06212
5200	+1·85	+2·63	0·6866	+0·06266
5000	+0·18	+2·70	0·6725	+0·06059
4916	+0·05	+2·53	0·6196	+0·06193
4800	+0·08	+1·65	0·4882	+0·05126

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PHOTOCHEMICAL REACTIONS WITH SOME INORGANIC COLLOIDS AS ACTIVE AGENTS UNDER THE INFLUENCE OF LIGHT IN VARIOUS STATES OF POLARISATION. PART XVI. PHOTOCHEMICAL REDUCTION OF CERIC TUNGSTATE SOL BY GLUCOSE

By T. Banerjee

Photochemical reduction of ceric tungstate sol by glucose has been investigated in dark and in light. Ceric content of the sol has been estimated.

The experimental arrangement is the same as discussed in Part I of this series (*J. Indian. Chem. Soc.*, 1937, **14**, 500).

Preparation of the Sol—An unstable colloidal solution of ceric tungstate is obtained when 0.5 g. of sodium tungstate, dissolved in 100 c.c. of distilled water are added while shaking to 100 c. c. of 6% aq. solution of ceric ammonium nitrate. This sol coagulated on standing for some time. On dialysis with distilled water (p_H near about 6), the coagulation is rather accelerated. But when dialysis is carried out with the help of a very dilute solution of HNO_3 (p_H 4) colloidal ceric tungstate, which remains stable for several days, is formed. The stability is due to a small amount of adsorbed ceric salt. And if this stabilising ceric salt is removed by adding a reducing agent, such as glucose or laevulose, which instanteneously reduces ceric salt in the dark, the sol coagulates immediately. Hence it is unsuitable for investigations on photochemical reactions especially photochemical reductions.

The stabilising ceric ion can, however, be replaced by a polyvent cation which is not easily reduced by glucose, laevulose etc. Thorium nitrate was chosen for the purpose. To 20 litres of distilled water is added 3 g. of thorium nitrate and the p_H is kept near about 4 by adding nitric acid. This constitutes the dialysing liquid. When the ceric tungstate sol prepared as usual, is dialysed with the above liquid, thorium ion gradually replaces stabilising ceric ion. When glucose is added to this dialysed sol, it no longer coagulates. This sol increases in viscosity very slowly and can be kept stable for months.

By a similar method ceric molybdate, vanadate etc. may be prepared and the process may be extended for the preparation of other complex ceric sols.

In this paper, we have studied the photochemical reduction of ceric tungstate by glucose.

The ceric content of the sol was estimated iodometrically. The results obtained were further checked by titration with the ferrous ammonium sulphate (*cf* Part VII).

Here also by passing pure nitrogen through the reaction mixture for a sufficiently long time, the induction period is much reduced and the photostationary state eliminated. No dark reaction was found between ceric tungstate and glucose for 6 hours. The light reaction was studied for 2 hours in all.

The velocity of reaction is given by $dx/dt = k (a-x)^{3/2}$ i.e. the velocity constant $k = 2/t. \left\{ \dfrac{1}{a-x} - \dfrac{1}{a} \right\}$ ...... (1)

TABLE I

Effect of varying the time.

Conc. of ceric tungstate (i.e. ceric equiva-
lent) $= 0.0168 M$. I_{abs} in ergs/cm²/sec $= 1350$
Conc. of glucose $= 5\%$. p_H 4·1.

Time after induction period.	Thiosulphate ($0·0025M$) for $0·23$ c.c. reaction mixture.	$k \times 10^5$	Quantum efficiency.
0 min	1·42 c.c.		
6	1·20	3·65	
120	1·08	3·34	2·0
		Mean 3·50	

TABLE II

Effect of varying the reductant conc.

Temp. $= 25°$. I_{abs}. in ergs/cm²/sec.
$= 1350$. Conc. of sol
$= 0·0168$ M. $p_H = 4·1$

Conc. of glucose	$k_1 \times 10^5$
10%	3·78
5	3·50
2·5	3·65

Under otherwise identical conditions, in presence of excess of reductant
the velocity of reaction is independent of the concentration of reductant.

TABLE III

Effect of varying the concentration of sol.

Temp. $= 25°$. I_{abs} in ergs/cm²/sec. $= 1350$
$p_H = 4·1$. Conc. of glucose $= 2·5\%$.

Conc. of sol.	$k_1 \times 10^5$
0·0168M	3·65
0·0278	3·76

TABLE IV

*Effect of varying the intensity of light
absorbed.*

Temp. $= 25°$. Conc. of sol $= 0·016M$. Conc.
of glucose $= 2·5\%$. $p_H = 4·1$.

I_{abs} in ergs/cm²/sec.	$k_I \times 10^5$
1350	3·65
690	2·50

From Table III it is evident that velocity of reaction is independent of
the concentration of the sol. From Table IV it appears that the velocity of
reaction varies as the square root of the intensity of absorbed radiation.

Temperature Coefficient of the Reaction.—The temperature coefficient
$k^{35°}/k_{25°}$ of the photoreduction is of the order of 1·1 — 1·3.

Quantum yield of the Photo-process.—The quantum efficiency of the
process was of the order of 2.

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TABLE V

Effect of polarised light.

Conc. of sol $= 0.0168 M$. Temp. $= 25°$. $p_H = 4.1$. Conc of Glucose $= 2.5\%$.

Nature of light in which the reaction was carried out.				Iabs in ergs/cm² /. sec.	$k_1 \times 10^5$	k_1 for 150 ergs /cm²/ sec.
Unpolarised	..	...	...	1350	3.65	1.22
l-Circularly polarised		...	...	150	1.25	
d-Circularly polarised		...	...	150	0.80	

From Table V it is noticed that $V_O = V_L = V_D$ the terms having the usual significance.

The mechanism of reaction is similar to that with ceric borate (Banerjee, *J. Indian Chem. Soc.*, 1945, 22, 102).

$$dx/dt = k_2 I_{abs} (a - x)^{3/2} = C_s$$

$$\text{Now } C_s = k' C_B / k'' + k' C_B$$

where C_B is the surface concentration of glucose and C_B, its bulk concentration.

When the reductant (glucose) is in excess, $k' + k C_B$ becomes practically equal to $K' C_B$ and the reaction becomes independent of the concentration of reductant under otherwise identical conditions. And this has been experimentally found to be the case.

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A NOTE ON THE ETHYLATION P-NITROPHENOL

By A. C. Roy and T. N. Ghosh

p-Nitrophenetole constitutes the starting material for the manufacture of phenacetin, an important synthetic drug, Nitrophenetole is generally prepared by heating the sodium salt of *p*-nitrophenol with ethyl chloride in an autoclave or with ethyl bromide at ordinary pressure.

The present investigation has been undertaken to see if the ethylation of *p*-nitrophenol can be successfully carried out by using ethyl hydrogen sulphate or ethyl potassium sulphate, both of which are cheaper than ethyl chloride or ethyl bromide. It has been found that ethyl hydrogen sulphate has very little action on *p*-nitrophenol and by using it, a very negligible yield of *p*-nitrophenetole is obtained (*vide* Experimental).

However, the use of ethyl potassium sulphate for ethylation on *p*-nitrophenol appears to be much more promising and under certain conditions *p*-nitrophenetole has been obtained in 71.5% yield. The results obtained are recorded in Table I.

TABLE I

20 G. of the sodium saet of *p*-nitrophenol and 100 c c. water were used in each experiment.

Expt. No.	Ethyl potassium sulphate.	Experimental condition.	Period of heating.	Yield of uncrystallised p-nitrophenetole	
				in gm.	percentage of theory
1	50 g.	Refluxing on wire-gauze	20 hrs.	2.6 g.	12.5
2	,,	,,	36	9	43.5
3	80	,,	20	7.4	35.7
4.	,,	,,	36	11.8	57
5	50	110—120° (autoclave)	7	6	29
6	,,	125—130° (autoclave)	7	9	43.5
7	80.	,, ,,	7	12.	58
8	,,	,, ,,	15.	14.8	71.5
9	,,	,, ,,	24	14.8	71.5

It is significant to note in this connection that when a mixture of equimolecular proportions of *p*-nitrophenetole and sodium-potassium sulphate in 20% alcohol is heated in an autoclave at 125-130° for 10 hours, no trace of *p*-nitrophenol is obtained.

E X P E R I M E N T A L

Action of Ethyl hydrogen Sulphate on p-*Nitrophenol*

(*a*) *p*-Nitrophenol (20 g.) was added to a .mixture of absolute alcohol (30 c.c.) and concentrated sulphuric acid (3.5 c c.), and the mixture was heated under reflux on the water-bath for 10 hours. Alcohol was then distilled under reduced pressure and the residue was cooled and diluted with water. The precipitated solid, after filtration, was triturated with excess of 5% aqueous caustic soda solution, filtered and washed thoroughly with water. A residue (0.4 g, 1.7% of theory) was left, which on crystallisation from alcohol, was proved to be *p*-nitrophenetole by mixed m.p. (58-60°) with a genuine sample.

(*b*) When the above reaction was carried out in a closed vessel at 80° for 10 hours, the yield of (uncrystallised) *p*-nitrophenetole came up to 1 g. (4.2% of theory).

(*c*) There was no formation of *p*-nitrophenetole when a mixture of of ethyl hydrogen sulphate (prepared as above, by mixing absolute alcohol with concentrated sulphuric acid in equimolecular proportions) and the sodium salt of *p*-nitrophenol was heated in presence of absolute alcohol on the water-bath for 10-12 hours.

(*d*) Ethyl hydrogen sulphate was prepared by treating ethyl potassium sulphate (112 g., prepared according to the method recorded in *Bull. soc. chim.*, 19, 295), suspended in alcohol (200 c.c.), with concentrated sulphuric acid (*d* 1.8, 37.2 c.c.) under. cooling. The mixture was filtered and the clear filtrate, mixed with *p*-nitrophenol (20 g.), was heated under reflux on the water-bath for 10 hours. Alcohol was then distilled off under reduced pressure and the residue was treated with an excess of 5% aqueous caustic soda solution[1] filtered and thoroughly washed with water. The residue (1.4 g, 5.8% of theory) was crystallised and proved to be *p*-nitrophenetole.

When the above reaction was carried out in an autoclave at 80° for 10 hours, the yield of (uncrystallised) *p*-nitrophenetole came up to 2·5 g. (10.4% of theory).

Action of Ethyl potassium sulphate on the sodium salt of p-*Nitrophenol*, —To a mixture of ethyl potassium sulphate (80 g.) and water (100 c.c.) was added the sodium salt of *p*-nitrophenol (20 g.). The resulting mixture was then heated in an autoclave at 125-130° for 16 hours. Subsequently the mixture was treated with an excess of 5% aqueous caustic soda solution and filtered. The residue was thoroughly washed with water and dried ; yield 14.8 g. (71.5% of theory). It was proved to be *p*-nitrophenetole.

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A LECTURE DEMONSTRATION OF OSMOSIS

.By Arcot Viswanathan

In a previous communication by the author, a lecture experiment on gas diffusion using Cartesian divers was described (*J. Indian Chem. Soc.,* 1934, 11, 79). The diver has been found also suitable for a demonstration of the phenomenon of osmosis as well.

A glass tube 18 cm. in length and 3.5 cm. in diameter or a short glass chimney, containing a molar solution of pure common salt or cane sugar, without air bubbles and with a coloured diver floating in it, is closed on one side by a semi-permeable membrane, and on the other by a rubber bung carrying a tap with a long stem of narrow bore (1.5 to 2 mm.). The diver, filled with the solution is retained above the tap, after removing any excess by loosening the tap key.

When the membrane part is dipped in pure water in a dish, with the tap open, and when leaks are absent, the solution rises quickly in the narrow tube, as the membrane used allows rapid osmosis. Some of the solution above the tap is now forced down by air from the lungs, until the diver acquires a density just insufficient for diving, and the tap is then closed. On surrounding the membrane alternately with pure water and a saturated solution of pure common salt (about 6 molar), the diver sinks down and then rises up, as a result of the direct and reversed osmosis produced. The experiment does not exceed ten minutes' time. Finally, with water in the dish and the tap open, the solution may be allowed to rise in the tube and overflow.

The membrane used is the tough and the transparent cellulose paper, taken from the wrappers of cigarette packets or other source. It is rinsed in spirit, soaked in distilled water for some hours, washed, and tied to the mouth of the tube with the edges closed over a layer of paraffin wax. Any possible leaks are stopped by an external coating of the paraffin.

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PHYSICO-CHEMICAL STUDIES OF COMPLEX ACID. PART I. DECOMPOSITION OF AMMONIUM MOLYBDATE WITH NaOH AND HCl

BY J. C. GHOSH AND ANIL BHUSAN BISWAS

The decomposition by HCl of a molybdic acid salt with a weak base (*i.e.* ammonium molybdate) has been studied electrometrically and otherwise and the results are compared with those of its salt with a strong base (*i.e.* sodium molybdate) under similar conditions. The nature of the decompositions is shown to be the same in both cases, higher and higher polysalts being formed with increasing addition of HCl. But the rapid rise of conductivity and (H$^+$) (hydrogen ion concentration) beyond the stage $R_2[O(MoO_3)_4]$ (R = Na or NH$_4$) is considered to be due to the formation of an acid molybdate $RH[O(MoO_3)_4]$. The action of NaOH on ammonium molybdate having the composition $(NH_4)_2$-$[O(MoO_3)_{2\cdot4}]$ has been studied electrometrically and it is shown that the anion of this salt gradually breaks into a normal one $[O(MoO_3)]$ and then NH$_4^+$ ion is displaced from the salt by Na$^+$ ion; from the curves, NH$_4^+$ ion can be estimated. The formation of higher polymolybdates from normal one has been described in terms of electronic structure.

A number of oxides such as silica, vanadium pentoxide, molybdenum and tungsten trioxides possesses definite acidic properties and forms normal salts, yet they exhibit abnormal changes during neutralisation of their acids or acidification of their normal salts.

The abnormal behaviour of sodium molybdate during acidification received the attention of the early workers. Thus Rosenheim and Bertheim (*Z. anorg. Chem.*, 1903, 34, 427 ; 1906, 54, 320) prepared the acid and acid salts from a normal sodium molybdate. Dumanskii and collaborators (*Kolloid Z.*, 1926, 38, 208) employed measurements of electrical conductivity and depression of freezing points to study the mode of displacement of the acid from sodium molybdate by HCl, while Britton and German (*J. Chem. Soc.*, 1930, 2154) studied its decomposition by strong and weak acids conductometrically and potentiometrically using quinhydrone electrode in the latter case. It appears from their results that in the acidified solution, sodium molybdate exists in the form of polymolybdates whose composition depends on the strength and concentration of the acid used. The polymolybdates formed after the stage $Na_2[O(MoO_3)_{4\cdot5}]$ are not stable towards HCl and undergo decomposition with the liberation of highly ionised polymolybdic acid in solution. But Jander and collaborators (*Z. anorg. Chem.*, 1930, 194, 413 ; *Metall-borse*, 1930, 20, 1855) from similar studies concluded that the salt, Na_2MoO_4, first goes over to a salt of trimolybdic acid followed by aggregates containing 6, 12, 24, etc. molybdenum atoms. Bevan (*Chem. Soc. Annual Reports*, 1943, p. 53) from glass electrode p_a and conductivity measurements showed that polymolybdates or tungstates of the type $R_2[O(MoO_3)_4]$ are salts of very strong acids. This is responsible for the polysalts not decomposing completely even in excess of HCl in dilute solutions.

The degree of decomposition, dissociation, hydrolysis etc. of a salt depend on the strength of the component acid and base on the one hand and [H$^+$] of the system on the other. The behaviours of sodium molybdate (*i.e.* salt of molybdic acid with a strong base) during acidification with strong and weak acids, as exhibited in electrometric studies, are known. It is desirable that the behaviour of a molybdic acid salt with a weak base

should be studied under similar conditions in order that more light may be thrown on the nature of the complex acid. Ammonium molybdate has been selected for the purpose, because it is not only the salt of a weak base but also, unlike Na$^+$ ion, it offers the additional advantage that the basic NH$_4$$^+$ ion associated at any stage with the acidic anion can be estimated by easy analytical method. Dhar and collaborators (Z. anorg. Chem., 1929, 174, 135 ; J. Indian Chem. Soc., 1932, 9, 441) in their work on " Dialysis, ultrafiltration and coagulation of molybdic acid sol " used ammonium molybdate and HCl or HNO$_3$ for the preparation of the sol, but its exact composition has not received attention.

EXPERIMENTAL

The potentiometric titration and p_H measurements were in all cases carried out with glass electrode prepared from corning glass No. 015 (MacInnes and Dole, J. Amer. Chem. Soc., 1930, 52, 29). A thin bulb showing interference colour only of this glass was blown at the end of a resistance glass tube and tested for its assymmetry E.M.F. and resistance. The one giving constant values of E.M.F. with buffer solutions and of resistance low enough for E.M.F. to be measured with an accuracy of ± 1.0 millivolts was selected for our experiments. The conductometric titration and conductivity measurements were done as usual using a drum roller meter-bridge (Leeds and Northrup). The temperature of the solutions was kept constant at 25° by immersing them into a thermostat while measurements were being made.

The reagents HCl and NaOH were C.P. grade quality and in making solutions, conductivity water was always used. The starting material, ammonium molybdate (B.D.H. pure) was recrystallised and analysed for its compositions. The ammonia content in the solution was estimated by the micro-Kjeldahl method and MoO$_3$ content by gravimetrically precipitating as MoS$_2$ and weighing as MoO$_3$ (Treadwell and Hall, " Analytical Chemistry", 1935, Vol. II, p. 274). The mean of five estimations are : NH$_3$, 8.42% and MoO$_3$, 80.0% ; ratio MoO$_3$/NH$_3$, 9.59. This percentage composition demands the formula of the material to be (NH$_4$)$_2$[O(MoO$_3$)$_{2.4}$], for which the value of the ratio MoO$_3$/NH$_3$ should be 9.6. A corresponding sodium salt of the same composition was isolated by Rosenheim (loc. cit.).

In the titrations three sets of readings were taken, all at 25° ; p_H or conductivity was measured after necessary addition of the titre in different glass stoppered bottles (i) immediately after proper mixing, (ii) after ageing for 48 hours at room temperature (25°), (iii) after boiling for 20 minutes at 85° and then cooling. Only readings from (i) and (iii) are represented in the graphs ; those from (ii) always assumed more or less intermediate values.

Reaction between Ammonium Molybdate and Caustic Soda.—In Fig. 1 (curves 1 and 1′) are represented the results obtained conductometrically by titrating 25 c.c. of ammonium molybdate solutions (6.0518 g. and 4.0412 g. per litre) with 0.665 N- and 0.33 N-NaOH respectively. The corresponding potentiometric titration results are shown similarly in Fig. 1 (curves 2 and 2′). Several such titrations of the molybdate at different concentrations varying from 2.0 to 10.0 g. per litre were carried out ; the respective curves were of the same nature as shown in Fig. 1. It may be noted here that ageing or heating the mixtures before taking readings had no appreciable influence on the course of any curves.

FIG. 1

Conductometric and potentiometric titrations of Am-molybdate with NaOH.

Decomposition of Ammonium Molybdate by Hydrochloric Acid.—In Fig. 2 (curve 1) are represented the potentiometric results obtained by titrating 50 c.c. of NH_4-molybdate solution (9.978 g. per litre) with 0.2956 N-HCl. In Fig. 2 (curve 2) are shown the corresponding conductometric results. The dotted lines show the course of readings taken after immediate mixing and the thick lines correspond to those recorded after heating and cooling at each stage. It will be noticed that the latter had the pronounced effect of making the inflexion sharp.

Dialysis of Acidified Ammonium Molybdate Solution.—To about 1000 c.c. of 0.2-0.3 M (with respect to MoO_3) solution of NH_4-molybdate, more than two equivalents of HCl diluted with water were added and after waiting for sometime the mixture dialysed in a parchment bag placed in a large porcelain basin, supplied with a current of distilled water at 50°. The presence of Cl' ion in the solution was tested with $AgNO_3$ solution acidified with HNO_3. After two days the sol in the bag was found to be free from Cl' ion. While the sol was under the process of further dialysis, some 40 c.c. sol were sampled out from the bag occasionally and analysed for its NH_3 and MoO_3 contents. This was continued for sometime until the concentration of MoO_3 in the sol was very low. The results are tabulated below.

Fig. 2

Conductometric and potentiometric titrations of Am-molybdate with HCl.

C.c. of 0.2956 N-HCl.

TABLE I

MoO₃ (in 25 c.c. sol).	Amount of NH₃.	Ratio $\dfrac{MoO_3}{NH_3}$.	Probable composition.
0.1151 g.	3.3140 × 10 g.	35.1	$(NH_4)_2[O(MoO_3)_{8\cdot5}]$ or $NH_4H[O(MoO_3)_{4\cdot25}]$
0.0925	2.8030	34.5	$(NH_4)_2[O(MoO_3)_{8\cdot1}]$ or $NH_4H[O(MoO_3)_{4\cdot05}]$
0.0698	1.9940	33.0	$(NH_4)_2[O(MoO_3)_{7\cdot8}]$ or $NH_4H[O(MoO_3)_{3\cdot9}]$
0.0339	0.9740	34.1	$(NH_4)_2[O(MoO_3)_{8\cdot1}]$ or $NH_4H[O(MoO_3)_{4\cdot05}]$
0.0231	0.6503	35.5	$(NH_4)_2[O(MoO_3)_{8\cdot8}]$ or $NH_4H[O(MoO_3)_{4\cdot9}]$

DISCUSSION

Reaction between NH₄-Molybdate and NaOH

Potentiometric studies (Fig. 1, curves 2 and 2′) show that in the very beginning there is a diffused inflexion, after which the p_{H} of the system changes only slowly with the addition of NaOH and finally terminates with a sharp inflexion. The course of the curve can be explained by assuming reactions to take place as follows :

(i) $(NH_4)_2[O(MoO_3)_{2\cdot4}] + 1.4H_2O = (NH_4)_2[O(MoO_3)] + 1.4H_2[O(MoO_3)]$.

(ii) $(NH_4)_2[O(MoO_3)_{2\cdot4}] + 2.8NaOH = (NH_4)_2[OMoO_3)] + 1.4Na_2[O(MoO_3)] + 1.4H_2O$.

The first diffused inflexion is due to the rapid removal of H^+ ions already present in the solution by the probable hydrolysis of the polymolybdate (i). As NaOH is gradually added, polymolybdic acid is liberated more and more to be neutralised forming normal sodium molybdate. This reaction becomes complete by the transformation of the poly-salt into a normal one. Further addition of NaOH increases the [OH'] considerably to show the sharp inflexion observed. That titre values corresponding to this sharp inflexion coincide with the stoichiometric amount demanded by (ii) above, and are shown in Table II below.

TABLE II

Mols. of $(NH_4)_2[O(MoO_3)_{2\cdot4}]$.	Mols. of NaOH (calc. from eqn. ii).	Mols. of NaOH corresponding to the final inflexion in curves.
5.923×10^{-4}	16.59×10^{-4}	16.38×10^{-4}
4.739	13.26	12.29
3.548	9.936	9.908
2.369	6.633	6.667
1.184	3.314	3.333

The corresponding conductometric studies (Fig. 1, curves 1 and 1') show that the conductivity of the solution begins to increase linearly in the beginning with gradual addition of NaOH and afterwards there is a nearly flat region of slight diminution of conductivities followed by sharp increase as would be done by free NaOH. Thus we observe here two breaks, the first one coincides with the final inflexion point of the corresponding potentiometric curve and obviously this must be associated with the end-point of the reaction represented by eqn. (ii). The flat portion is evidently due to the formation of slower moving ions in the solution resulting from the addition of NaOH. This can be ascribed to the reaction :

(iii) $(NH_4)_2[O(MoO_3)_{2\cdot4}] + 4.8NaOH = 1.4Na_2[O(MoO_3)] + Na_2[O(MoO_3)] + 2NH_4OH + 1.4H_2O.$

After reaction shown in eqn. (ii) is over, double decomposition between NaOH and $(NH_4)_2[O(MoO_3)]$ begins to take place, when NH_4^+ ion, associated with the molybdate ion, is displaced by Na^+ ion from NaOH. We have seen previously that the p_H of the system increases considerably when the reaction (ii) was over and as such the liberated weakly basic NH_4^+ ion will remain completely unionised. Thus the part previously played by the faster moving NH_4^+ ion (mobility at 25° is 74.8) in conducting current,

TABLE III

Mols. of $(NH_4)_2[O(MoO_3)_{2\cdot4}]$	Mols of NaOH calc. by eqn. (iii).	Mols. of NaOH from 2nd break in curves.	Mols. of NaOH equiv. to the diff. between 1st and 2nd breaks.	Calc. mols. of NH_3 in soln.
5.923×10^{-4}	28.43×10^{-4}	29.26×10^{-4}	12.62×10^{-4}	12.51×10^{-4}
4.739	22.74	22.78	10.09	10.02
3.548	17.03	17.22	7.49	7.508
2.369	11.37	11.09	5.06	5.008
1.184	5.68	5.61	2.48	2.505

was taken over by the slower moving Na^+ ion (mobility at 25° is 50.1). During this process of substitution of NH_4^+ ion by Na^+ ion, the resulting conductivity of the solution diminishes. When it is over, still further addition of NaOH causes conductivity to increase considerably. If so, the added NaOH equivalent to the 2nd break here should be equal to the stoichiometric amount demanded by eqn. (iii), as shown in Table III above. The difference between the 1st and 2nd breaks can alternatively be taken as equivalent to the amount of NH_4^+ ion present in the solution.

It will be noticed that the amount of NaOH equivalent to the 2nd break agrees well with the amount calculated from eqn. (iii) and also the difference between the 1st and 2nd breaks fairly equals the calculated amount of NH_4^+ ion present in the solution. It was also observed that the titration of the same NH_4-molybdate solution with NaOH using phenolphthalein as indicator showed the same end-point as the final inflexion or 1st break of the respective potentiometric and conductometric titrations.

Decomposition of NH_4-Molybdate with HCl

Potentiometric studies (Fig. 2, curve 1) show that $[H^+]$ slowly increases in the beginning and then rapidly with an inflexion near about p_H 3.0. If it is assumed that HCl added has gone into complete reaction, the composition of the molybdate at the point of inflexion will be $(NH_4)_2[O(MoO_3)_{4.2-4.5}]$. The corresponding conductometric studies (Fig. 2, curve 2) similarly demonstrate that there is no appreciable change of conductivities in the beginning until the composition of the molybdate corresponds to $(NH_4)_2[O(MoO_3)_{4.5}]$ and thereafter there is a rapid and uniform increase as would be the case with free HCl.

The course of the curves is interpreted as follows :—when HCl is added to NH_4-molybdate solution, the partly liberated molybdic acid in the solution is immediately taken up by the parent salt left unreacted to form a polymolybdate, thus,

$$x(NH_4)_2[O(MoO_3)] + 2xHCl = 2xNH_4Cl + xMoO_3 . H_2O.$$
$$(NH_4)_2[O(MoO_3)] + xMoO_3 . H_2O = (NH_4)_2[O(MoO_3)_{x+1}] + xH_2O.$$

The value of x in the complex will depend on the $[H^+]$ of the solution. The polymolybdates that are formed in the beginning have got the same conductivity as their parent salts and this is true until the composition of the salt becomes $(NH_4)_2[O(MoO_3)_{4.5}]$, when still more HCl was added, the conductivity and $[H^+]$ of the resulting solution increased rapidly.

Starting with Na-molybdate under similar conditions, Dumanskii and collaborators (loc. cit.) found that after the addition of 1.6 moles of HCl per mole of Na_2MoO_4, there was sudden increase in the difference between the freezing point depression of actual reaction mixture and of a theoretical mixture made up on the assumption of simple double decomposition. Britton and German (loc. cit.) also starting with Na_2MoO_4 and HCl got similar inflexions electrometrically after the composition $Na_2[O(MoO_3)_{4.5}]$ was reached, and they assumed that the sodium tetramolybdate was decomposed by HCl liberating the corresponding acid $H_2[O(MoO_3)_4]$ which ionised strongly in solution to show increased conductivity. But Jander and collaborators (loc. cit.) came to somewhat different conclusions.

In the case of Na-molybdate it was shown that the specific conductivities at the same dilutions of the molybdate varying from Na_2O, MoO_3 to $Na_2O, 4MoO_3$, do not differ appreciably from each other but for still higher polysalts the values appear to be much greater as shown in Table IVA below, where the specific conductivities of the solutions of the solid salts at different dilutions at 25° are reproduced from Britton and German (loc. cit.) [these data being compiled by them from the records of Walden (Z. physikal. Chem., 1887, 1, 529), Rosenhein (Z. anörg. Chem., 1916, 96, 139) and Rosenhein, Felix and Pinkser (ibid., 1913, 79, 292]. In Table IVB are given the corresponding data on equivalent conductivity as calculated by the author. The dilutions (in litres) refer to volumes containing 1 g. atom of sodium.

TABLE IVA

Dilution	32	64	128	256	512	1024
$Na_2[O(MoO_3)]$	3.14	1.66	0.87	0.45	0.23	0.12
$Na_2[O(MoO_3)]_{12/5}$	3.09	1.70	0.91	0.49	0.26	0.14
$Na_2[O(MoO_3)]_4$	3.09	1.69	0.94	0.51	0.28	0.16
$Na_2[O(MoO_{38})]$ (?)	6.15	4.74	2.73	1.48	0.79	0.40

TABLE IVB

	Dilution	32	64	128	258	512	1024
(1)	$Na_2[O(MoO_3)]$	100.5	106.3	111.4	115.2	117.8	122.8
(2)	$Na_2[O(MoO_3)]_{12/5}$	98.9	108.7	116.5	125.4	133.1	143.2
(3)	$Na_2[O(MoO_3)]_4$	98.9	108.1	120.3	130.5	143.4	163.9
(4)	$Na_2[O(MoO_3)]_8$ (?)	196.8	303.4	349.4	378.8	404.4	409.7
	or $NaH[O(MoO_3)_4]$						
	Diff. (4)—(3)	97.9	195.3	229.1	248.3	261.0	245.8

In the above table the conductivities of the salts up to the tetramolybdate have nearly the same value but the supposed octamolybdate has considerably higher value. It will be noticed that the difference between the equivalent conductivities of the tetra- and octa-molybdates, except at the dilution 32, assumes values which will be obtained if one H^+ ion is generated in the solution of the Na-tetramolybdate at the expense of Na^+ ion (the difference between the ionic mobilities of H^+ and Na^+ at 25° is 349.7—50.1, i.e., 299.6).

From this it appears that the composition of the solute, which was supposed by Britton and Rosenheim as Na-octamolybdate, should more reasonably be represented as NaH-$[O(MoO_3)_4]$. The salt isolated, and designated as $Na_2[O(MoO_3)_8]$ and used for measurements of electrical conductivity by Rosenheim and Felix (loc. cit.) was obtained from an acidified solution of sodium molybdate. This should be represented by the alternative formula $NaH[O(MoO_3)_4]$. As a matter of fact Rosenheim and collaborators (loc. cit.) thought that it could be represented as an acid salt $NaH\ Mo_4O_{13}$.

Accordingly we must ascribe the considerable increase in conductivity and $[H^+]$ after the composition $Na_2[O(MoO_3)_{4.5}]$ or as in the present case of $(NH_4)[O(MoO_3)_{4.5}]$, to the formation of an acid molybdate corresponding to RH $[O(MoO_3)_4]$ where R=Na

or NH_4. The analytical results (Table I) for the composition of the solute of the molybdate acid sol after careful purification by dialysis, show that the value of this ratio MoO_3/NH_3 obtained, can definitely be associated with the formula $NH_4H[O(MoO_3)_4]$. Thus molybdic acid sol, as we have obtained under the stated conditions, contains the acid molybdate partly in molecularly dispersed state, *i.e.* in true solution and partly in polymerised or aggregated state as micelle ions or colloidal particles of the composition $\{NH_4H[O(MoO_3)_4]\}_n$.

In keeping with the electronic theory of valency we can picture the decomposition of normal molybdate by an acid to form gradually higher polymolybdate, thus,

$$R\begin{bmatrix} & O & \\ & \uparrow & \\ O-&Mo&-O \\ & \downarrow & \\ & O & \end{bmatrix}R \rightarrow R\begin{bmatrix} O & & O \\ \uparrow & & \uparrow \\ O-Mo&-O-&Mo-O \\ \downarrow & & \downarrow \\ O & & O \end{bmatrix}R \rightarrow R\begin{bmatrix} O & & O \\ \uparrow & & \uparrow \\ O-Mo&-(O-&Mo)_n-O \\ \downarrow & & \downarrow \\ O & & O \end{bmatrix}R$$

Salt of normal molybdic acid.   Salt of bimolybdic acid.   Salt of higher polymolybdic acid, where n may be 2, 3, 4, etc.

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PHYSICO-CHEMICAL STUDIES OF COMPLEX ACID. PART II. CONDUCTO-METRIC AND GLASS ELECTRODE TITRATION OF MOLYBDIC ACID SOL

By J. C. GHOSH AND ANIL BHUSAN BISWAS

Molybdic acid sol, prepared by the action of dilute hydrochloric acid on ammonium molybdate solution, when dialysed free from Cl' ion, has a composition of the solute corresponding to $NH_4H[O(MoO_3)_4]$. The sol on dilution from 3.30×10^{-2} M-MoO_3 to 1.65×10^{-4} M-MoO_3 gave continually increasing value of p_H. In the region of p_H 3.8 to 4.5, the curve was rather flat and this has been ascribed to the disintegration of colloidal micelle of molybdic acid to true solution containing simpler ions as $HMoO_4'$ etc. The dissociation constant of this acid ion $HMoO_4'$ has been calculated to be $p_k = 6.33$ from the potentiometric titration curve of the sol with NaOH.

Though molybdenum and tungsten occur in the same group of the periodic table as sulphur and chromium and form well defined normal salts as Na_2MoO_4, the corresponding molybdic and tungstic acids do not resemble H_2SO_4 or H_2CrO_4 in any other respects, and show abnormal changes in p_H and conductivity during neutralisation.

Travers and Malaprade (*Bull. soc. chim.*, 1929, **39**, 1406, 1543) investigated the course of neutralisation of molybdic acid solution with KOH electrometrically and suggested the presence of tetramolybdic acid in solution from the observation of an inflexion in the curve at 1/4 equivalent of the acid. Bevan (Britton, "Hydrogen Ions", 1940, Vol. I, p. 224) came to the same conclusion from similar electrometric studies and assumed the acid ionising as,

$$H_2[O(MoO_3)_4] \rightleftharpoons [O(MoO_3)_4]'' + 2H^+$$

$$[O(MoO_3)_4]'' + 3H_2O \rightleftharpoons 4 MoO_4'' + 6 H^+$$

during neutralisation. Chatelain (*Compt. rend.*, 1939, **208**, 584) got the same nature of curves as Travers (*loc. cit.*) and Honnelaitre (*Ann. Chim.*, 1925, **3**, 31) but interpreted her results on the assumption that dimolybdic acid in solution ionised thus,

$$Mo_2O_7H_2 \rightleftharpoons [Mo_2O_7H]' + H^+$$

$$[Mo_2O_7H]' \rightleftharpoons [Mo_2O_7]'' + H^+$$

The above mechanism supported her previous works on the absorption spectra of MoO_3 solution (*Compt. rend.*, 1937, **205**, 222; 1938, **206**, 669) when the presence of only one kind of molybdate ion responsible for absorption was found.

The apparently controversial ideas, as revealed, are due to the fact that the polyphasic character of the system was not taken into consideration; it was thought that the equilibrium of the system in all stages of reaction was governed by the law of mass action as applicable to homogeneous systems. The investigations of Rosenheim and Bertheim (*Z. anorg. Chem.*, 1903, **34**, 427; 1096, **54**, 320) and Dhar and collaborators (*Z. anorg. Chem.*, 1929, **184**, 135) have shown that molybdic acid in its aqueous solution is present partly as a colloid and partly as true solution and Dhar and collaborators (*J. Indian Chem. Soc.* 1943, **20**, 282) grouped it as "colloidal electrolytes" due to its similarity in behaviour with soap solution (McBain, 1920). The carefully dialysed molybdic

acid salt, as we have obtained under conditions stated in Part I, was found by ultramicroscopic examination to contain a considerable number of colloidal particles (10^9 per c.c. for 0.02 M-MoO$_3$ sol) and the mean composition of the solute was shown to correspond with the formula NH$_4$H[O(MoO$_3$)$_4$]. The likely equilibrium condition existing can possibly be represented as :— .

$$n\text{NH}_4\text{H}[\text{O}(\text{MoO}_3)_4] + x[\text{O}(\text{MoO}_3)_4]'' \rightleftharpoons [\text{NH}_4\text{H}[\text{O}(\text{MoO}_3)_4]_n[\text{O}(\text{MoO}_3)_4'']_x$$

Simple molecules   Micelles or
in solution   colloidal particles.

The measurement of conductivity and [H$^+$] at different dilutions of the sol may indicate the existence and the nature of transformation of such equilibrium. .

Following Duclaux (*J. chim. phys.*, 1909, **7**, 405), Michaelis (*Biochem. Z.*, 1920, **106**, 83), Pauli and Valkó (" Electrochemie der Kolloide", 1929) and McBain (*J. Amer. Chem. Soc.*, 1920, **42**, 426 ; *J. Phys. Chem.*, 1924, **28**, 706) we are led to believe that colloidal solutions of electrolytic substances should be treated as counterparts of electrolytes in true solution and equilibrium condition arising in any stage of the system is governed by the law of mass action just like substances in true solution. But Mukherjee and collaborators (*Trans. Nat. Inst. Sci. India*, 1937, **1**, 227) questioned the validity of such assumptions in certain cases and illustrated the difficulties encountered in the studies of a number of colloidal systems like silicic acid, palmitic acid, MnO$_2$ etc., and some sparingly soluble organic acids like cinnamic acid, etc., in interpreting the electrometric titration curves of such heterogeneous acid systems. Accordingly the electrometric titration curves should be analysed and interpreted with caution paying the due attention to the polyphasic character of the system.

The object of the present investigation is to study critically the course of electrometric titration curves of the neutralisation of molybdic acid sol with NaOH, and to determine the nature of its ionisations at different stages.

<center>EXPERIMENTAL</center>

The conductometric and glass electrode titration methods were the same as described in Part I (*this issue*, p. 228). The preparation of a well-dialised molybdic acid sol from NH$_4$-molybdate and HCl was also described there. The effect of ageing for 48 hours or heating at 85° for 20 minutes after each addition of NaOH was also observed as before.

<center>*Conductometric and Potentiometric Titrations*</center>

In Fig. 1 (curve 1) are represented graphically the results of conductometric titration of 50 c.c. of 2.545×10^{-2} M-MoO$_3$ sol (according to gravimetric estimation) with 0.703 N-NaOH. The corresponding potentiometric results are shown similarly in curve 2. The dotted lines represent the course when readings were taken immediately after mixing of the added titre, the continuous lines being for readings taken after heating and cooling to 25°. The data from the ageing experiments are not shown because they have more or less intermediate values.

It will be noticed that heating after each addition of the titre influences the course of the curves only in the first portion but later both types of curves coincide. In curve 2, it is seen that p_H values rapidly increase in the beginning as if free H$^+$ ions are being

FIG. 1

Conductometric titrations of molybdic acid sol with NaOH.

The 1st inflexions are approximately 1/7 of the 2nd inflexion values in all cases. The volumetric titration with the same amount of the sol, carried out separately using phenolphthalein as indicator, showed that the titre values coincided with the 2nd inflexion values. Leaving the question of the 1st inflexion for later discussion, the reaction of the solute of the MoO_3 sol with NaOH, corresponding to 2nd inflexion, can be represented by the following stoichiometric equation,

removed; after that the curve shows slightly undulating region; beyond that it assumed the nature of the neutralisation of a weak acid ending with a sharp inflexion. We, thus, observe here two inflexions and the data from a number of such titration curves are given in Table I.

TABLE I

Mols of MoO_3 present.	Mols of NaOH corresponding to		Calc. Mols of NaOH from eq. (i).
	1st inflexion.	2nd inflexion.	
4.243×10^{-4}	1.10×10^{-4}	7.60×10^{-4}	7.425×10^{-4}
7.065	2.00	12.60	12.36
8.875	2.35	15.85	15.43
12.790	3.37	22.29	22.38
17.820	4.95	32.10	31.19

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(i) $2NH_4H[O(MoO_5)_4] + 14NaOH \longrightarrow (NH_4)_2[O(MoO_5)] + 7Na_2[O(MoO_3)] + 8H_2O.$

The NaOH equivalent calculated from this equation agreed well as shown in Table I.

Referring to the corresponding conductometric curve in Fig. 1 (curve 1) it is found that conductivity diminishes rapidly in the beginning, passes through a sharp minimum and then it increases to a maximum, followed by a small, nearly flat region where conductivity tends to diminish and then again increases very rapidly as would be the case if free NaOH were present. We, thus, observe here 3 breaks, our experimental data corresponding to the three breaks are given in Table II.

TABLE II

Mols of MoO$_3$.	Mols of NaOH calc from eqn. (ii)	Mols of NaOH from			Diff. between 3rd and 2nd breaks.	Estimated Mols of NH$_3$ (Kjeldahl method).
		1st break.	2nd break.	3rd break.		
4.243×10^{-4}	8.486×10^{-4}	1.15×10^{-4}	7.50×10^{-4}	8.55×10^{-4}	1.05×10^{-4}	1.062×10^{-4}
7.065	14.13	1.90	12.50	14.40	1.90	1.760
8.872	17.74	2.25	15.75	18.80	2.05	2.22
12.79	25.58	3.30	22.28	25.35	3.07	3.20
17.82	35.64	4.50	31.50	36.10	4.60	4.45

FIG. 2

p_H of MoO$_3$ sol at diff. dilutions.

Comparing these values with those in Table I, it is seen that the 1st and 2nd breaks fairly coincide with the 1st and 2nd ineflxion values of the potentiometric curves. Obviously their occurences are due to the same reaction, the existence of the 2nd break is to be associated with equation (i) above. The observed flat region and the 3rd break can be represented by an equation,

(ii) $2NH_4H[O(MoO_3)_4] + 16NaOH \longrightarrow 7Na_2[O(MoO_3)] + Na_2[O(MoO_3)] + 2NH_4OH + 8H_2O.$

The NaOH equivalents calculated from this equation, as seen in Table II, agree well with the values from 3rd breaks. Moreover, the amount resulting from the difference between the 3rd and 2nd breaks should be equivalent to the quantity of NH_3 present in the solution. These calculated values are actually of the same order as those estimated by the Kjeldahl method.

p_H of MoO_3 Sol at different Dilutions

The carefully purified sol (0.033 M-MoO_3) is diluted with conductivity water to different extents in separate glass-stoppered bottles and allowed to stand for 48 hours at room temperature (25°). The p_H values are then measured and the results are presented graphically in Fig. 2, where the p_H values of the diluted sols are plotted against the log of different dilutions.

DISCUSSION

If we assume that molybdic acid in sols or solutions ultimately behaves as dibasic $H_2[O(MoO_3)]$ during neutralisation, two moles of NaOH per atom of molybdenum are necessary for complete neutralisation. The potentiometric and conductometric results (Tables I and II) showed definitely that 7/8 of the total Mo was available for neutralisation as normal dibasic acid forming $Na_2[O(MoO_3)]$ and the rest remained associated with the NH_3 present in the sol as $(NH_4)_2[O(MoO_3)]$. When still more NaOH was added, reaction took place as

$$(NH_4)_2[O(MoO_3)] + 2NaOH \rightarrow Na_2[O(MoO_3)] + 2NH_4OH.$$

It will be seen in Tables I and II that the 1st inflexion or break of the respective potentiometric or conductometric curves occurs roughly when one mole of NaOH per mole of $NH_4H[O(MoO_3)]$ was added and this can be qualitatively represented by an equation,

$$NH_4H[O(MoO_3)_4] + NaOH \rightarrow NH_4Na[O(MoO_3)_4] + H_2O.$$

The region of the potentiometric curve beyond the 1st inflexion is due to the process of transformation of the polyacidic anions existing as colloidal particles or micelles into simpler ones and this extends until the alkali equivalent to the one-half of the acid available for neutralisation, is added. The solution at this stage and after, contains the acid molybdate ion ($HMoO_4'$) in true solution (near about p_H 5.0) and with further addition of NaOH, the curve assumes the nature of the neutralisation of a weak acid. The nature of ionisations during the 1st half of the neutralisation curve can be represented as follows :

$$H[O(MoO_3)_4]' \rightleftharpoons H^+ + [O(MoO_3)_4]''$$
$$3H_2O + [O(MoO_3)_4] \rightleftharpoons 3[HMoO_4'] + 2H^+$$

Mukherjee (loc. cit.) analysed the applicability of the relationships existing in the case of true solution to heterophase systems and found the mass law to be inapplicable in such cases since the mass of the acid in the interior of the colloidal particles or micelles are unavailable for equilibrium with the dissolved acid in the intermicellar liquid and the kinetics of the surface reaction was found to play a definite role. Therefore, the degree

of dissociation, dissociation constant, solubility and similar other magnitudes have a sense different from that in true electrolytic systems. Accordingly, it is meaningless to attempt to determine the reaction equilibrium as indicated in the above or to suggest, as was done by previous workers, the presence of any definite polyacid such as tetra or dimolybdic acids from inflexions or breaks observed in electrometric curves so long as the system is heterogeneous. But beyond p_H 5.0, *i.e.* in the 2nd half of the potentiometric curve, we can safely assume the applicability of the mass law for the reaction equilibrium

$$H\,MoO_4{}' \rightleftharpoons H^+ + MoO_4{}''$$

when

$$K = \frac{[H^+][MoO_4{}'']}{[HMoO_4{}']}\,.$$

In Table III below we have calculated some of the p_k values from the potentiometric titration curve in the region above p_H 5.0.

<div align="center">TABLE III</div>

NaOH.	$p_H.$	$p_k.$
1.10 equiv.	5.38	6.33
1.15	5.50	6.32
1.20	5.62	6.33
1.25	5.67	6.25
1.30	5.79	6.16

The p_k values are fairly constant showing the validity of our assumptions.

The p_H-dilution curve reveals how high molecular colloidal polymolybdic acid gradually goes into true solution. The p_H values remain almost steady, like a buffer solution when the dilution is increased from 200 to 2000 times. With progressive dilution in this region (p_H 3.8, concentration of the MoO_3 sol $1.65 \times 10^{-4} M$) p_H values change much more slowly than would be expected from an acid in true solution, because of the transformation of colloidal polymeric anions into simpler ones which generate H^+ in the process. This process becomes complete, *i.e.* practically all the particles pass into true solution after dilution to 2000 times (p_H 4.5, concentration of the sol $= 1.65 \times 10^{-5}$ M-MoO_3). As the dilution is increased further, values of p_H increase as would be the case with a weak acid.

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CRYSTALLINE COMPONENTS OF THE BARK OF *PRUNUS PUDDUM* (ROXB), PART II. ON THE CONSTITUTION OF PRUNUSETIN

By Dukhaharan Chakravarti and Chandranath Bhar

A compound, m.p. 237-38°, has been isolated in 0.08 per cent yield from the ethereal extract of the bark of *Prunus puddum*. It has been named *Prunusetin* and has been shown to be 5-methoxy-7 : 4′-dihydroxy-*iso*flavone. On demethylation with hydriodic acid it′ yields a trihydroxy compound identical with the natural *iso*flavone genistein.

In Part I (*J. Indian Chem. Soc.*, 1944, **21**, 171) of this series of investigations puddumetin isolated from the bark of *Prunus puddum*, has been shown to be 7-methoxy-5 : 4′-dihydroxyflavone identical with genkwanin isolated by Nakao and Tseng (*J. Pharm. Soc. Japan*, 1932, No. 602, 343 ; 1933, No. 608, 905) from a Chinese drug ' Yuen-Hua.'

This paper deals with the constitution of the second compound, which has been named *prunusetin*. It crystallises from ethyl acetate and glacial acetic acid as pale yellow shining needles, m.p. 237-38°.

Analytical data of prunusetin are in agreement with the formula $C_{16}H_{12}O_5$ and hence it is isomeric with puddumetin. It is soluble in caustic alkali with a permanent deep yellow colour. Ferric chloride imparts a brown-violet coloration showing the presence of phenolic-OH group. It contains two OH groups as it easily forms a colorless diacetyl derivative, m.p. 220-22°. Methoxyl estimation by Zeisel's method indicates the presence of one OMe group and hence prunusetin may be written as $C_{15}H_7O_2(OMe)(OH)_2$.

Prunusetin is insoluble in alkali carbonate and bicarbonate. From the yellow alkaline solution the original substance is recovered on acidification. These properties and the molecular formula of the compound suggest a chromone structure for prunusetin, namely (I).

(I)

Prunusetin remains unaffected when air is aspirated through its alkaline solution for three hours. On methylation with methyl iodide it produces a dimethyl ether, m.p. 160-61°, which is insoluble in alkali and cannot be further acetylated. When prunusetin is demethylated with hydriodic acid for one hour in an atmosphere of dry carbon dioxide, a trihydroxy compound, m.p. 291-93°, is isolated which is found to be identical in all respects with the natural *iso*flavone genistein (II) (Perkin and Newbary, *J. Chem. Soc.*, 1899, **75**, 830 ; Perkin and Horsfall, *ibid.* 1900, **77**, 1310 ; Baker and Robinson, *ibid.*, 1928, 3115), the coloring matter of Dyer's Broom. The derivatives of the demethylated product are identical with those of genistein described in the literature (Baker and Robinson, *J. Chem. Soc.*, 1925, **127**, 1981).

TABLE I

	Demethylated product of prunusetin. m.p. 291-93°	Genistein, m.p. 291-93° (synthetic).	Mixed m.p. 292-93°
Triacetyl derivative	202-203°	197-201°	201
Dimethyl ether	139-40°	137-39°	
Acetylated dimethyl ether	201-203°	202-204°	
C-methylated dimethyl ether	201-202°	200-201.5°	
Trimethyl ether	160-161°	160-62°	161°

(II)

Prunusetin is thus a monomethoxy derivative of genistein and is isomeric with the natural *iso*flavone, prunetin (III) or (IV) (Finnemore, *Pharm. J.*, 1910, **31**, 604 ; Baker and Robinson, *J. Chem. Soc.*, 1928, 1022) isolated from *Prunus serotina*. It is not, however, identical with prunetin as shown below.

TABLE II

	Prunetin. m.p. 242°	Prunusetin, m.p. 237-38°
Diacetyl derivative	m.p. 224-26°	220-22°
Monomethyl ether (which forms an acetyl derivative)	145°	No monomethyl derivative is formed
Dimethyl ether (which does not form an acetyl derivative)	The formation of dimethyl ether is not recorded in literature	m.p. 160-61°

Since Prunusetin readily forms a dimethyl ether, which does not contain a free hydroxyl group, it seems likely that it has a methoxyl group in position 5 and its probable constitution is (V) though according to Bose and Nath (*J. Indian Chem. Soc.*, 1938, **15**, 141 ; *cf.* Shah, Virkar, Venkataraman, *ibid.*, 1942, **19**, 135) a benzopyrone with a methoxyl group in position 5 does not usually occur in nature.

(III)

(IV)

(V)

For want of sufficient material, prunusetin could not be hydrolysed in quantity, but in a trial experiment a ketone, forming a semicarbazone, was obtained in traces. Experiments towards the synthesis of prunusetin in support of the structure (V) are in progress.

EXPERIMENTAL

The powdered bark (600 g.) was extracted with ether (16 hours). The brown ethereal extract was concentrated to about one-tenth of its volume and kept overnight. The yellow solid which separated out was filtered and the filtrate was freed from the solvent. A brown oil was obtained which solidified on keeping to a gelatinous mass.

Isolation of Prunusetin.—The yellow solid obtained above was a mixture of two substances, one being less soluble in alcohol than the other, crystallised first from alcohol as yellow needles, m.p. above 270°. The more soluble fractions crystallised from alcohol as light yellow needles, m.p. 224-30°. The latter on repeated crystallisation from glacial acetic acid melted at 237-38°(A). Variation of solvent such as ethyl acetate, nitrobenzene did not raise the melting point. From acetic acid mother-liquor was obtained a pale yellow solid, m.p. 224-26°(B).

The gelatinous mass obtained above was treated in a similar manner as described in Part I (Chakravarti and Ghosh, *loc. cit.*). Light brown crystals, m.p. 224-30°, were obtained. These together with the fraction (B), obtained above, were just dissolved in boiling ethyl acetate and allowed to stand overnight. First two or three crops of crystals had the melting point above 270°. The ethyl acetate mother-liquor on evaporation gave a solid which crystallised from glacial acetic acid as pale yellow shining needles, m.p. 237-38°, identical with the product (A), the total yield being 0.08% of the weight of the dry bark.

Prunusetin (5-methoxy-7 : 4'-dihydroxy*iso*flavone) is soluble in alcohol, ethyl acetate, sparingly soluble in ether, benzene, and insoluble in chloroform. It is readily soluble in cold caustic alkali solutions with yellow colour, but it is insoluble in alkali carbonate and bicarbonate. An alcoholic solution of the substance gives the brown-violet coloration with ferric chloride. It produces no coloration when its alcoholic solution is reduced with magnesium and hydrochloric acid in the cold. [Found in a sample dried over P_2O_5 in vacuum at 110-15° : C, 67.56 ; H, 4.02 ; OMe, 10.87. $C_{15}H_9O_4(OMe)$ requires C, 67.61 ; H, 4.22 ; OMe, 10.92 per cent].

Diacetylprunusetin (5-methoxy-7 : 4'-diacetoxy*iso*flavone) was obtained by gently refluxing prunusetin with acetic anhydride and two drops of dry pyridine. After one hour the mixture was cooled, diluted with water, heated on a boiling water-bath for a few minutes and allowed to stand. The white solid was collected, washed with water and crystallised from rectified spirit as white shining plates, m.p. 220-22°. [Found in a sample dried over P_2O_5 at 110-15° in vacuum : C, 65.33. H, 4.65 ; $C_{19}H_{13}O_6(OMe)$ requires C, 65.21 ; H, 4.31 per cent].

Prunusetin dimethyl ether (7 : 5 : 4'-trimethoxy*iso*flavone) was prepared by refluxing for 2 hours a solution of prunusetin (0.1 g.) in dry acetone with methyl iodide (10 c.c.) in presence of anhydrous potassium carbonate (2 g.). The mixture was filtered, the filtrate evaporated to dryness, and the residue crystallised from dilute alcohol as colourless needles

m.p. 160-61°. It is found to be identical with genistein trimethyl ether (mixed m.p.). [Found in a sample dried over P_2O_5 at 100° in vacuum : C, 69.00 ; H, 5.05 ; OMe, 28.78. $C_{15}H_7O_2(OMe)_3$ requires C, 69.23 ; H, 5.12 ; OMe, 29.81 per cent].

Attempted Acetylation of Prunusetin Dimethyl ether.—The above dimethyl ether was refluxed with acetic anhydride and pyridine in the usual manner. The solid crystallised from rectified spirit as colourless needles, m.p. 160-61° (mixed m.p. with prunusetin dimethyl ether 160-61°).

Attempted aerial oxidation of Prunusetin.—Air was aspirated through an aqueous caustic potash solution of prunusetin for 3 hours and the solution was kept overnight. On acidification the solid was collected and crystallised from glacial acetic acid as pale yellow needles, m.p. 237-38° (mixed m.p. with prunusetin 237-38°).

Demethylation of Prunusetin with Hydriodic acid : Isolation of Genistein.—Prunusetin (0.1 g.) was heated for 1 hour at 130-35° in a glycerine bath with hydriodic acid (sp. gr. 1.7, 10 c.c.) in an atmosphere of dry carbon dioxide. The mixture was cooled and diluted with water. The separated solid was filtered, washed with sodium thiosulphate solution, then with water and crystallised from dilute alcohol as colorless shining needles, m.p. 291-93° (and mixed m.p. with synthetic genistein). (Found in a sample dried over P_2O_5 at 115-20° in vacuum : C, 66.63 ; H, 4.04. Calc. for $C_{15}H_{10}O_5$: C, 66.67 ; H, 3.7 per cent).

Triacetylgenistein.—The demethylated product (0.1 g.) was acetylated in the usual manner. The product crystallised from dilute alcohol as colourless shining flakes, m.p. 202-203°. [Found in a sample dried over P_2O_5 at 105-10° in vacuum : C, 63.60 ; H, 4.15. Calc. for $C_{21}H_7O_5(COCH_3)_3$: C, 63.63 ; H, 4.04 per cent].

C-methylated genistein dimethyl ether (6-methyl-7 : 4'-dimethoxygenistein) was obtained by refluxing for 3 hours a solution of the demethylated product in dry acetone with methyl iodide and anhydrous potassium carbonate in the usual manner. The reaction mixture was freed from the solvent and the residue crystallised from dilute alcohol as silky needles, m.p. 201-202°.

Genistein Dimethylether (7 :- 4'-dimethoxy-genistein).—An ice-cooled solution of the demethylated product (0.1 g.) in absolute alcohol (Ca-dried) was treated with a cold ethereal solution of diazomethane (3 mol.) in dry ether and the mixture was kept overnight. Ether was removed, the mixture neutralised with acetic acid and diluted with water. The solid separating was filtered, washed with water and crystallised from dilute alcohol as coulorless shining needles, m.p. 139-40°. (Found in a sample dried over P_2O_5 in vacuum at 90-95° : C, 68.10 ; H, 4.80. Calc. for $C_{17}H_{14}O_5$: C, 68.45 ; H, 4.73 per cent).

Acetylgenistein dimethyl ether (5-acetoxy-7 : 4'-dimethoxyisoflavone).—The above dimethyl ether was acetylated with acetic anhydride and pyridine in the usual manner. The product crystallised from dilute alcohol as shining plates, m.p. 202-204°.

All analyses recorded in this paper are microanalyses carried out by Mr. N. Ghosh, to whom our best thanks are due.

ON THE HEAT POLYMERISATION OF CASTOR OIL

By Supravat Mukherjee and B. K. Mukherjee

Castor oil polymerises at a fairly low temperature. It is observed that the increase in molecular weight is nearly 2 to 3 times its original value when the oil is heated for 4 hours at 100°. The oil is partly dehydrated and the Diene value increases within the range investigated.

The viscosity and specific gravity increase fairly proportionately with the increase in molecular weight. The process of polymerisation does not take place by simple doubling of molecules but is rather irregular as is evidenced by the increase in molecular weight which does not take place in simple multiples of the original oil.

Goswami and Saha (*J. Indian Chem. Soc.*, 1937, **14**, 1116) have shown that when boiled oil is prepared from linseed oil in presence of catalysts the olein and linolein of linseed oil at first form hydroxy compounds, which subsequently yield unsaturated compounds by elimination of water and finally give compounds having double bonds in conjugated positions.

The recinoleic acid glyceride in castor oil on the other hand will directly lose a water molecule to form such compounds

$$CH_3(CH_2)_5CH(OH)CH_2CH=CH(CH_2)_7COO—$$

$$\xrightarrow{(-H_2O)} CH_3(CH_2)_5CH=CH—CH=CH(CH_2)_7COO—$$

$$\text{or}\quad CH_3(CH_2)_4CH=CH\text{-}CH_2—CH=CH(CH_2)_7COO—$$

by re-arrangement $\quad CH_3(CH_2)_5CH=CH—CH=CH(CH_2)_7\ COO—$

Synthetic drying oils with properties approaching to those of Tung oil have been prepared by abstracting a molecule of water from the castor oil molecule (Good, *Chem. Eng. News*, 1944, **18**, 21) when, as indicated above, compounds having the molecular characteristics of Tung oil *i.e.* compounds containing double bonds in conjugated positions, are produced.

Now, once the conjugated system is introduced in the molecule it may be expected that it would take the course of typical butadiene polymerisation as follows :

$$-CH=CH-CH=CH-\qquad \begin{array}{l} -CH-CH=CH-CH- \\ \quad | \qquad\qquad\quad | \\ -CH-CH=CH-CH- \end{array}$$

The present paper is an attempt to study the course of polymerisation of castor oil when this oil is heated to moderately low temperatures.

EXPERIMENTAL

The castor oil used was cold pressed in the laboratory, filtered and dried over anhydrous sodium sulphate. Three sets of experiments were carried out at three different temperatures varying the duration of heating in each case. The temperatures inves-

tigated were 50°, 75° and 100° and in every case the oil was heated for 1, 2, 3 and 4 hours respectively.

The prepared samples were then examined under the following heads : specific gravity, refractive index, viscosity, iodine value, Diene value, acetyl value and molecular weight.

The refractive index was observed at 40° with a Butyro-Abbe refractometer. The viscosity of the samples was measured in a Redwood viscosimeter and results are expressed both in Redwood and Absolute units.

The Diene value or the maleic anhydride number, which is a measure of conjugated linkages in the system, was determined by the method of Kaufmann as modified by Baltes and Buter (*Ber.*, 1937, **70B**, 903).

The molecular weight which indicates the state of polymerisation was found by the Beckmann's freezing point depression method in a benzene solution of the oil.

The results are recorded in Tables I and II.

<center>TABLE I</center>

Oil heated for	Original oil.	Refractive index			Original oil.	Iodine value after heating at		
		50°.	75°.	100°.		50°-	75°.	100°.
0 hrs.	69.8	—	—	—	83.8	—	—	—
1		70.2	70.55	71.36		83.9	85.55	87.3
2		70.5	70.95	71.6		85.3	86.2	87.9
3		70.7	71.1	72		85.7	86.5	88.73
4		70.95	71.35	72.45		86.2	87.2	89.75

<center>TABLE II</center>

	Condition.	Acetyl value.	Diene value.	Iodine value.
1.	Original oil	145	2.95	83.8
2.	Oil heated for 4 hrs. at 50°	136.8	6.4	86.2
3.	,, ,, at 70°	128.2	11.91	87.2
4.	,, ,, at 100°	117.8	28.2	89.75

The decrease in acetyl value accompanied by a simultaneous increase in iodine value and Diene value established the validity of our assumption, namely on heat treatment water molecules are eliminated at the expense of OH groups in recinoleic acid glycerides with simultaneous increase in unsaturation.

It is also observed by plotting the relationship between (*a*) I.V. and refractive index (Fig. 1), (*b*) I.V. and acetyl value, and (*c*) iodine value and Diene values (Fig. 2) that (*i*) the variation of refractive index with iodine value is a linear one ; (*ii*) the Diene value increases as the iodine value of the sample increases and (*iii*) the acetyl value does not increase proportionately with the increase in iodine value. The break in this curve might be explained thus : At the initial stage, loss of moisture from the recinoleic acid glyceride causes a decrease in acetyl value but subsequently there is a formation of hydroxy acids from olein and linolein (present to the extent of about 10% in castor oli). These

FIG. 1   FIG. 2

two phenomena counteract each other in such a manner that the fall in acetyl value is less than what would be expected from the rise in iodine value. After a while, however, the curve becomes regular which supports the view expressed regarding the course of chemical action taking place during the heating *i.e.* the hydroxy acid formed gives up a molecule of water and molecules with conjugated double bonds are finally produced by rearrangement.

The development of conjugated system in accordance with the theoretical assumption is thus verified.

The extent of polymerisation of the oil molecules will be manifested from Table III which shows increased values for specific gravity, viscosity and molecular weight of the oil samples after heat treatment.

TABLE III

Temp.	Time of heating (hrs.)	Sp. gr.	Red-wood (seconds)	Viscosity (poise)	Mol. wt. I	Mol. wt. II	Average value Mol. wt.
	Original	0.9572	1312	3.41	854	857	856
	1	.9573	—	—	864	866	865
	2	.9576	1336	3.47	912	916	914
50°	3	.9581	1350	3.77	995	997	996
	4	.9590	1585	4.12	1047	1050	1049
	1	0.9585	1490	3.87	918	920	919
75°	2	.95968	1592	4.14	1046	1050	1048
	3	.9604	1608	4.18	1136	1139	1138
	4	.9609	1652	4.27	1235	1240	1238
	1	0.96092	1658	4.30	1250	1252	1251
100°	2	.9616	1742	4.53	1395	1392	1348
	3	.9620	1884	4.89	1602	1600	1601
	4	.9629	2105	5.47	1840	1845	1843

The relation between the molecular weight and Diene value is shown in Fig. 3. Since the increase in molecular weight is not in simple multiples of the original oil, it can be

concluded that the polymerisation of the glycerides does not take place regularly and by a simple doubling of molecules as in ordinary polymerisation reactions in organic chemistry but that the glycerides are first decomposed into fatty acids and lower glycerides and the liberated fatty acid molecules then undergo polymerisation. This, however, requires substantiation by further experimental evidence. Determination of the acid value might throw some light on this point.

FIG. 3

The results obtained reveal that by gradual heating there is a considerable increase in unsaturation in the molecule and also a corresponding regular increase of molecular weight. Whilst progressive polymerisation is evidenced by the gradual increase in molecular weight, similar changes in iodine value and Diene value indicate simultaneous development of conjugated system in the molecule. With prolonged heating at higher temperatures it is to be expected therefore, that the polymerisation will be extensively marked and would result in the ultimate formation of a highly viscous rubber-like mass when the Diene value will abruptly fall. Further experiments are being conducted to illustrate these points.

The authors acknowledge their grateful thanks to Prof. M. N. Goswami for the valuable suggestions and continued interest during the progress of the work.

QUINOLINE-8-CARBOXYLIC ACID AS AN ANALYTICAL REAGENT. PART II

By Anil Kumar Majumdar

In a previous paper (*J. Indian Chem. Soc.*, 1941, **18**, 419) it was shown that quinoline-8-carboxylic acid can be used as a reagent for the estimation of copper between p_H 2.78 and 7.0, copper being completely precipitated. In presence of acetic acid, however, it was found that good results were obtained either by adding a few grams of sodium acetate, or a large excess of the sodium salt of the reagent, as the copper salt of quinoline-8-carboxylic acid was found like copper quinaldinate (Majumdar, *Analyst*, 1939, **64**, 874 ; 1943, **68**, 242) to show specific solubility in acetic acid, independent of p_H. In presence of mineral acid at a lower p_H value copper is completely precipitated but in presence of acetic acid even at a higher p_H the precipitation is incomplete.

It has now been found that cadmium and iron (ous) also form salts of similar composition as that of copper. On adding sodium salt of the reagent to a well cooled solution of ferrous salt containing Rochelle salt or hydroxylamine hydrochloride, a red colouration (pale red to dark red depending upon the concentration of iron) is obtained, the intensity of which increases with the addition of potassium cyanide. The colour given by quinaldinic acid under similar condition is, however, more intense ; moreover, quinoline-8-carboxylic acid gives only a red compound and no *cis-trans* isomers (*cf.* Rây and Bose, *Z. anal. Chem.*, 1933, **95**, 400).

Using sodium salt of the reagent it is found that copper can be separated from arsenic, antimony, and bismuth in presence of Rochelle salt and also from cobalt and zinc in weakly acid solution. The results of these experiments are given below.

Experimental

Salts of Quinoline-8-carboxylic Acid

Cadmium Salt.— To an acid solution of cadmium salt was added an excess of a solution of sodium salt of the reagent. The cold solution was neutralised with dilute caustic soda solution till just alkaline (using bromothymol blue indicator). The precipitate which separated on stirring was filtered, washed with cold water and dried at 110°. On analysis the salt was found to contain 25% of cadmium and 5.8% of nitrogen (micro analysis). The compound $(C_{10}H_6O_2N)_2Cd$ requires 24.6% of cadmium and 6.1% of nitrogen.

Ferrous Salt.— On adding an excess of a solution of sodium salt of the reagent to that of ferrous ammonium sulphate containing Rochelle salt a dark red solution was obtained. This on cooling overnight was found to give a violet-red crystalline precipitate which was filtered, washed with cold water, dried in air and analysed. [Found : N (micro analysis), 6.73 ; Fe, 13.2. The compound $(C_{10}H_6O_2N)_2Fe,H_2O$ requires N, 6.7 ; Fe, 13.4 per cent].

Separation of Copper from Arsenic, Antimony, Bismuth, Cobalt and Zinc.—To a solution of copper containing arsenic, antimony or bismuth a few grams of

Rochelle salt (2-4 g.) were added. The mixture was neutralised (using bromothymol blue indicator) and treated with a few c.c. of $N/10$- sulphuric acid. To the solution after dilution an excess of sodium salt of the reagent (1 g. of quinoline-8-carboxylic acid per 100 c.c. solution) was added with stirring. After cooling the precipitate was filtered through a gooch crucible, washed with cold water, dried at 150° and weighed.

In presence of cobalt or zinc, copper was estimated in the same way except that no Rochelle salt was added and the solution was heated to boiling both before and after the addition of the reagent. This was then quickly cooled with stirring, and the precipitate was filtered.

TABLE I

Weight of copper used $= 0.01907$ g.

Other metals.	$N/10$-H_2SO_4.	Reagent.	Total vol.	Weight of copper. ppt.	found	Error
0.105 g. As	4 c.c.	20 c.c.	150 c.c.	0.1221 g.	0.01903 g.	—0.00004 g.
0.0105 ,,	5	20	150	0.1223	0.01906	—0.00001
0.042 ,,	5	20	150	0.1226	0.01911	0.00004
0.021 ,,	7	20	150	0.1221	0.01903	—0.00004
0.0521 Bi	4	20	150	0.1222	0.01905	—0.00002
0.1042 ,,	4	20	150	0.1225	0.01909	0.00002
0.1563 ,,	5	20	150	0.1224	0.01908	0.00001
0.2084 ,,	5	20	150	0.1229	0.01915	0.00008
0.0510 Sb	4	20	150	0.1226	0.01911	0.00004
0.1020 ,,	4	20	150	0.1222	0.01905	—0.00002
0.1530 ,,	5	20	150	0.1226	0.01911	0.00004
0.0285 Co	7	25	150	0.1227	0.01913	0.00006
0.0570 ,,	7	25	180	0.1230	0.01917	0.00010
0.0570 ,,	10	25	300	0.1222	0.01905	—0.00002
0.3018 Zn	10	25	300	0.1229	0.01915	0.00008
0.1509 ,,	10	25	300	0.1227	0.01913	0.00006

The copper solution and the solution of the reagent used in the above series of experiments were the same as was used in Part I (*J. Indian Chem. Soc.*, 1941, **18**, 419), and all other reagents and chemicals used were of "pro-analyse" variety of Kahlbaum.

My best thanks are due to Prof. P. Ray for the facilities received in working out this piece of work in his laboratory.

APPLICATION OF HAMMICK AND ANDREWS EQUATION TO TERNARY MIXTURES. PART II

By W. V. BHAGWAT AND S. O. SHUKLA

Hammick and Andrews' equation is applicable to ternary mixtures of laevulose, urea, monochloroacetic acid and acetamide in water.

In a previous paper Bhagwat and Shukla (*J. Indian Chem. Soc.*, 1944, 21, 179) have shown that the parachor of a ternary mixture is given by the expression

$$P_m = (1-x-y) P + xP_x + yP_y$$

where the symbols have their usual significance. The values assumed for P_x and P_y in considering the application of the above mixture law are the values observed in solution by us, and not the calculated values.

The average value for the parachor of acetamide in aqueous solution is 130, while for urea it is about 118 (*loc. cit.*). The values for monochloroacetic acid and laevulose as observed are given below. Parachor of water has been taken to be 52.3.

TABLE I

Parachor of laevulose

Temp.	$x=0.01509.$ d	$M_m=20.44$ r	P_m	P_x	$x=0.0215,$ d	r	$M_m=21.48$ P_m	P_x
25°	1.05	65.61	56.02	296.2	1,071	69.15	57.82	307,1
30	1.048	67.92	55.97	294.9	1.069	68.39	57.8	306.3
40	1.046	67.45	55.99	292.9	1.066	67.61	57.79	305.3
50	1.043	66.83	56.03	296.9	1.063	66.68	57.75	304.0

Parachor of monochloroacetic acid

Temp.	$x=0.0550$ d	$M_m=22.21$ r	P_m	P_x	$x=0.0726$ d	r	$M_m=23.56$ P_m	P_x
25°	1.080	48.84	54.23	86.7	1.106	47.69	55.99	102.5
30	1.081	48.31	54.18	85.8	1.104	47.21	55.93	101.9
40	1.078	47.75	54.18	85.8	1.101	46.72	55.97	102.3
50	1.075	47.32	54.19	86.0	1.098	46.34	56.01	102.8

TABLE II

A. Laevulose, monochloroacetic acid and water

(a) 1.6154 g. of laevulose+3.1298 g. of monochloroacetic acid+10.2842 g. of water. x (Laevulose) =0.0144. y (Monochloracetic acid)=0.0544. $(1-x-y)=0.9312.$ $M_m=24.49.$

Temp.	d	r	P_m	P_x
25°	49.25	1.123	57.77	300
30	48.75	1.121	57.73	297.5
40	47.64	1.117	57.73	297.5
50	47.21	1.113	57.68	293

(b) 1.574 g. of laevulose +4.224 g. of monochloroacetic acid+10.214 g. of water. $x=0.140.$ $y=0.0720.$ $(1-x-y)=0.9140.$ $M_m =25.79.$

d	r	P_m	P_x
1.141	47.66	59.37	296.5
1.138	47.1	59.39	298
1.132	46.45	59.46	303
1.127	55.71	59.5	305

(c) 2.3002 g. of laevulose+4.268 g. of monochloroacetic acid+10.28 g. of water. $x=0.0202.$ $y=0.716.$ $(1-x-y)=0.9082.$ $M_m=26.78.$

Temp.	d	r	P_m	P_x
25°	1.154	48.14	61.12	309.1
30	1.51	47.64	61.12	309.1
40	1.147	46.77	61.08	304.2
50	1.142	46.34	61.19	312.6

(d) 2.302 g. of laevulose+3.126 g. of monochloroacetic acid+10.32 g. of water. $x=0.0205.$ $y=0.054.$ $(1-x-y)=0.9261;$ $M_m=25.44.$

d	r	P_m	P_x
1.136	49.39	59.34	305
1.134	48.74	59.27	300.7
1.129	48.08	59.33	303.9
1.124	47.53	59.41	307.8

TABLE II (contd.)

B. Urea, monochoroacetic acid and water.

6.0456 g. of urea+3.117 g. of monochloroacetic acid+10.366 g. of water. $x=0.1423$. $y=0.0437$. $(1-x-y)=0.8140$. $M_m=27.6$.

Temp.	d	r	P_m	P_x
25°	1.148	55.24	65.2	126.3
30	1.145	54.7	65.54	126.4
40	1.140	53.83	65.57	120.5
50	1.134	52.72	65.57	120.5

C. Laevulose, urea and water.

1.6408 g. of urea+10.486 g. of water. $x=0.0131$. $y=91464$. $(1-x-y)=0.84$. $M_m=26.28$.

d	r	P_m	P_x
1.1305	60.77	64.94	116.4
1.127	60.12	64.92	116.3
1.123	59.02	64.85	115.9
1.118	57.94	64.85	115.9

D. Acetamide, monochlorocetic acid and water.

6.1442 g. of acetamide+4.3012 g. monochloracetic acid+10.26 g. of water. $x=0.1426$. $y=0.0634$. $(1-x-y)=0.7940$. $M_m=28.84$.

Temp.	d	r	P_m	P_x
25°	1.164	52.3	66.62	130.1
30	1.160	51.05	66.55	129.6
40	1.155	50.12	66.61	130.1
50	1.147	49.43	66.67	130.5

E. Acetamide, laevulose and water.

6.1516 g. of acetamide+2.2924 g. of laevulose+10.3076 g. of water. $x=0.1490$. $y=0.01846$. $(1-x-y)=0.83252$. $M_m=27.26$.

d	r	P_m	P_x
1.144	71.01	69.15	140.0
1.140	70.15	69.2	140.5
1.136	69.18	69.2	140.5
1.131	68.23	69.26	140.9

In case of A the parachor of laevulose has been calculated by ternary mixture law, in B and C that of urea has been found, while in D and E the values are calculated for acetamide. It will be seen that the observed results fairly agree with the values of these substances as obtained by us in aqueous solutions.

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ESTIMATION OF BISMUTH. PART VII. GRAVIMETRIC ANALYSIS WITH PHENYLARSONIC ACID

By Anil Kumar Majumdar

Further investigations have been carried out on the conditions and limits of precipitation of Bi, separation of Bi from thallous salts and alkaline earths as well as on the composition of the Bi compound.

In Part I of this series (*J. Indian Chem. Soc.*, 1944, **21**, 119) gravimetric methods for the estimation of bismuth in presence of a large number of ions with the reagent phenylarsonic acid have been described. A tentative formula $C_6H_5AsO_3$, BiOH for the bismuth compound of the reagent was suggested. Results of further investigations on the composition of the bismuth compound, the conditions of precipitations and the precipitation limit for bismuth, and the separation of bismuth from alkaline earths and thallous salts have been reported in the present paper.

EXPERIMENTAL

Composition of the Bismuth salt of Phenylarsonic Acid.—The precipitate obtained by following either of the procedures I and II described in Part I (*loc. cit.*), after being well washed with hot water, was dried at 110-120° to a constant weight. A weighed amount was decomposed by boiling with caustic soda solution. Arsenic in the filtrate was precipitated and estimated as As_2S_5. From the residue bismuth was estimated as Bi_2O_3. (*i*) 0.2586 g. gave 0.1398 g. Bi_2O_3 whence Bi = 48.49 per cent. (*ii*) 0.1914 g. gave 0.1037 g. Bi_2O_3 and 0.0686 g. As_2S_5, hence Bi = 48.6; As = 17.3 per cent. Further 0.1569 g. of substance on combustion gave 0.1024 g. of CO_2 and 0.0231 g. of H_2O, from which C = 17.8; H = 1.64 per cent.

 requires C, 16.9; H, 1.41; As, 17.6; Bi, 49.06 per cent.

Precipitation limit for Bismuth.—Very dilute solutions of bismuth of concentrations ranging from one part of bismuth in 10,000 parts and more of water were examined. To 10 c.c. solution a few drops of the reagent and ammonium acetate were added and gently heated. Distinct precipitates were observed up to 1 part of bismuth in 2,050,000 parts of water. Solutions of greater dilution produced opalescence.

Reagent.—In the following experiments reagents and chemicals used were the same as was used previously (*J. Indian Chem. Soc.*, 1944, **21**, 119).

Standard solutions.—Bismuth solution was prepared in the same way as in Part I (*loc. cit.*). Solutions of calcium, barium and magnesium nitrates were prepared from their respective carbonates (proanlyse of Kahlbaum) and that of strontium from nitrate (pure quality of Kahlbaum); the strength of the solutions being determined by the usual methods. For thallium, Merck's pure thallous sulphate was used, and thallium in the solution was determined as thallous iodide.

Separation of Bismuth from Alkaline Earth Salts.—The method outlined under Procedure II in Part I (*loc. cit.*) was followed and the results obtained are given below in Table I.

TABLE I

Metals taken.		Reagent added	Weight of bismuth		Error
			ppt.	found	
Bi	0.0391 g.	15 c.c.	0.0796 g.	0.0390 g.	—0.0001 g.
Ca	0.0213				
Ba	0.0355				
Mg	0.0152				
Sr	0.023				
Bi	0.0391	15	0.0794	0.0389	—0.0002
Ca	0.0426				
Ba	0.0710				
Mg	0.0304				
Sr	0.046				

Separation of Bismuth from Thallous Salts.—As the sulphate of thallium was used, the procedure followed was exactly the same as described in Part I (*loc. cit.*) for the estimation of bismuth in presence of sulphate ions. Results appear in Table II.

TABLE II

	Metals taken	Reagent added	Wt. of Bi ppt.	Bi found	Error
Bi	0.0391 g.	15 c.c.	0.0795 g.	0.0390 g.	—0.0001 g.
Tl	0.1228				
Bi	0.0391	15	0.0797	0.0391	Nil
Tl	0.0611				

Critical Studies in the Conditions of Precipitation

A critical study was made to establish the conditions under which bismuth may be completely precipitated and thus may be separated from other elements. The following tables show some of the results of a large number of trial experiments carried out for the purpose.

During the estimation of bismuth in presence of ammonium acetate and acetic acid it was found that the quantity of the reagent required to precipitate bismuth should be at least three times the amount of bismuth present (*cf.* experimental procedure, pp. 121-122 in Part I, *loc. cit.*). The results in Table III show the effect of variation.

TABLE III

No.	Bi taken.	Reagent added.	Total vol.	Weight of bismuth		Error
				ppt.	found	
*1	0.0250 g.	5 c.c.	200-250 c.c.	..	..	..
*2	0.0250	5	200-250	..	..	..
**3	0.0250	5	200-250	0.0478 g.	0.0234 g.	—0.0016 g.
**4	0.0250	5	200-250	0.0480	0.0235	—0.0015
5	0.0300	10	200-250	0.0612	0.0300	Nil
6	0.0300	10	200-250	0.0610	0.0299	—0.0001
7	0.0300	10	200-250	0.0610	0.0299	—0.0001
8	0.0250	10	200-250	0.0508	0.0249	—0.0001
9	0.0250	15	200-250	0.0510	0.0250	Nil

*Precipitate gelatinous, very difficult to filter and wash.

**In presence of 20 c.c. ammonium acetate, about 4 to 5 c.c. of acetic acid (2N) were rembred to make the precipitate crystalline but low results were still obtained.

It was also observed that on the addition of sodium acetate to a bismuth solution containing just enough nitric acid to prevent hydrolysis, the bismuth was completely precipitated with a nearly stoichiometric quantity of the reagent (*cf.* experimental procedure, p. 121 in Part I, *loc. cit.*). The following data were obtained.

TABLE IV

No.	Bi taken.	Reagent added.	Sodium acetate.	Total vol.	Weight of bismuth		Error.
					Bi ppt.	Bi found.	
1	0.0250 g.	10 c.c.	20 c.c.	200-250 c.c.	0.0510 g.	0.0250 g.	Nil
2	0.0250	10	10	200-250	0.0512	0.0251	0.0001 g.
3	0.0300	10	10	200-250	0.0612	0.0300	*Nil*
4	0.0250	5	10	200-250	0.0512	0.0251	0.0001
5	0.0250	5	10	200-250	0.0508	0.0249	—0.0001
*6	0.0250	3	10	200-250	..	..	..
*7	0.0250	3	10	200-250	..	..	..
8	0.0250	3.5	5	200-250	0.0512	0.0251	0.0001
9	0.0250	3.5	5	200-250	0.0510	0.0250	Nil

*Precipitate did not become crystalline.

Further it was found that if the solution contains just sufficient nitric acid (dilute) to keep bismuth in solution, the metal can be completely precipitated by the reagent without the addition of sodium acetate. But the solution should be boiled for about 25 to 30 minutes to make the precipitate crystalline. The precipitate thus obtained requires a long time, preferably overnight, to settle; moreover, under this condition bismuth cannot be separated from a large number of elements. With excess of acid low results were obtained.

TABLE V

No.	Bi taken.	Reagent added.	Total vol.	Weight of bismuth		Error.
				ppt.	found.	
*1	0.0685 g.	20 c.c.	170 c.c.	0.1395 g.	0.0684 g.	—0.0001 g.
*2	0.0250	10	200-250	0.0512	0.0251	0.0001
*3	0.0250	10	200-250	0.0512	0.0251	0.0001
†4	0.0685	15	350	0.1345	0.0660	—0.0025
†5	0.0685	15	350	0.1322	0.0649	—0.0036
‡6	0.0685	15	170	0.1336	0.0655	—0.0030

* The filtrate on testing with H_2S was found to be free from bismuth.

† The solution contained about 3 c.c. of conc. HNO_3 and the filtrate was found to contain bismuth (with H_2S).

‡ The solution contained about 10 c.c. of normal nitric acid and the filtrate was found to contain bismuth (with H_2S).

Bismuth can also be completely precipitated from a solution which was just neutralised with ammonia (using Wesselow's indicator) after the addition of the reagent and acidified with a few drops (4 to 6) of dilute acetic acid (2N) as shown below. Also under this condition bismuth cannot be separated from a large number of elements.

TABLE VI

No.	Bi taken.	Reagent added.	Total vol.	Weight of bismuth		Error.
				ppt.	found.	
1	0.0250 g.	3.5 c.c.	200-250 c.c.	0.0510 g.	0.0250 g.	Nil
2	0.0250	3.5	200-250	0.0512	0.0251	0.0001 g.
3	0.0250	3.5	200-250	0.0512	0.0251	0.0001

It may be remarked that the conditions outlined in the experimental procedures given in Part I (*loc. cit.*) for the gravimetric estimation of bismuth are the best that could be obtained, as they are by no means too rigid for an experimenter carrying out a rapid estimation. Other salient features may also be noted :

(*i*) Boiling for 5 to 7 minutes with stirring is enough to give good crystalline precipitate which settles quickly and can be very easily filtered and washed within 15-20 minutes.

(*ii*) It enables the separation of bismuth from a large number of elements.

(*iii*) The complete estimation, involving precipitation, filtration, washing and drying, never requires more than an hour and a half.

My best thanks are due to Prof. P. Ray for the facilities received in working out this piece of work in his laboratory.

STUDIES IN GLASS SYSTEMS : X'RAY ANALYSIS OF KCl DISSOLVED IN B₂O₃-GLASS

By Subodh Kumar Majumdar and Ranendra Mohon Palit

Further experimental evidence is adduced in support of the fact, first noticed by the authors that the spacing of polar crystals is enlarged when they are dissolved in a homogeneous glass. In the p ᵍ sent paper, the spacing of KCl dissolved in boric oxide glass has been investigated and an enlargement of the spacing to the extent of about 36% over the normal value has been noticed. An tentative theory of the phenomenon is given.

Majumdar and Palit (*J. Indian Chem. Soc.*, 1942, 19, 461) were the first to notice that a polar crystal like NaCl, when dissolved in a glass like boric oxide, still retained its crystalline form but the spacing was enlarged to the extent of over 60% of the normal value. According to the theory of polar crystals first put forward by Born and Lande (*Verhand. deuts. physikal. Gesellschaft*, 1918, 20, 210) and modified later by various workers, like London, Lennard Jones, Slater and Kirkwood and others, the equilibrium in a polar crystal is assumed to be the result of several forces, mainly two, namely the electrostatic or Coulomb forces between the oppositely charged ions, which obey the inverse square law and the short distance repulsive forces, which involve power of the radius higher than the two. The theoretical considerations in calculating lattice energy are all based upon the assumption that the medium intervening the charged particles in the crystal is a vacuum. In other words, the dielectric constant is taken as unity.

EXPERIMENTAL

As in the experiment with NaCl, recrystallised and dried KCl was mixed with specially dehydrated B_2O_3 and heated in a platinum crucible in an electric furnace for eight to ten hours until a thoroughly homogeneous melt was obtained. The crucible was then chilled when the melt cracked on solidification. The particles were taken out and the chlorine content volumetrically determined. Another sample was powdered and the Debye-Scherer photograph was taken in the usual way.

Potassium metaborate was prepared according to the directions of Rosenheim and Leyer (*Z. anorg. Chem.*, 1921, 119, 1). About 18 g. of KOH and 64 g. of boric acid were dissolved in 45 c.c. of warm water. On cooling the solution in a freezing mixture, about 34 g. of the salt, KBO_2, separated out. These crystals were dissolved in 30 c.c. of hot water and recrystallised. In this way about 11 g. of the pure salt were obtained. X-ray measurements were done in the same way as in the case of NaCl—B_2O_3 system (Majumdar and Palit, *loc. cit.*). An exposure of about twelve hours was given and the films developed. Fig. 1, 2, 3, 4, 5 represent respectively the photographs with pure KCl, KBO_2 and three samples of KCl—B_2O_3 system.

As in the case with NaCl, B_2O_3 partly reacted with KCl forming KBO_2 as indicated by common lines leaving considerable amounts of KCl dissolved in the glass. The percentage of KCl found by analysis corresponds to this dissolved chloride.

In the case of KCl reflections from odd planes are absent. Therefore the values Sin $\theta/\sqrt{4}$, Sin $\theta/\sqrt{8}$, Sin $\theta/\sqrt{12}$, Sin $\theta/\sqrt{16}$, etc. are calculated and the two constant values corresponding to K_a and K_β determined by trial. The lines due to the borate are eliminated by reference to its photograph. The value of a_0 is then calculated.

The following tables give the results of analysis of the different systems.

TABLE I

A. KCl (Fig. 1)

Intensity	W	S	W	S	V.W.	S	W	W	V.W.
x	3.85	4.21	5.42	6.03	6.7	7.45	8.7	9.82	10.9

B. KBO$_2$ (Fig. 2)

Intensity	W	W	W	W	W	W	W
x	2.35	2.9	3.6	3.8	4.2	4.8	5.25

TABLE II

A. KCl (7.2%) dissolved in B$_2$O$_3$ (Fig. 3)

Intensity	S	W	W	S	S	S	W
x	2.35	2.7	2.87	3.3	3.65	3.82	4.0
Intensity	W	S	S	W	W	W	
x	4.2	4.4	4.76	5.23	5.55	6.3	

B. KCl (7.81%) dissolved in B$_2$O$_3$ (Fig. 4)

Intensity	S	W	W	S	S	S	W	S	W	W	W
x	2.35	2.65	2.9	3.3	3.65	3.85	3.98	4.2	4.42	4.8	5.2

C. KCl (8.13%) dissolved in B$_2$O$_3$ (Fig. 5)

Intensity	S	W	W	S	S	S	S	S	W	W
x	2.35	2.7	2.9	3.3	3.6	3.8	4.4	4.8	5.55	6.3

In the photographs of KCl dissolved in B$_2$O$_3$, the lines due to KBO$_2$ are eliminated by referring to Table I B and the spacing of dissolved KCl calculated.

With pure KCl K_a is found to be 0.1264 and for K_β 0.1151. Hence a_0 for pure KCl works out with

$$K_a, \ a_0 = \frac{1.539 \times 10^{-8}}{2 \times 0.1264} = 6.075 \ \text{Å} \ ; \qquad K_\beta, \ a_0 = \frac{1.389 \times 10^{-8}}{2 \times 0.1151} = 6.040 \ \text{Å},$$

the mean value being 6.056 Å. This is in agreement with the standard value 6.2 Å.

In the case of KCl dissolved in B$_2$O$_3$ glass, the spacing of the former is found to be almost independent of the salt concentration in the region of concentration investigated, and the constant is found to be 0.0942 with K_a and 0.0833 with K_β. Hence a_0 for KCl dissolved in B$_2$O$_3$ works out

$$\text{with} \quad K_a, \ a_0 = \frac{1.539 \times 10^{-8}}{2 \times 0.0942} = 8.163 \ \text{Å} \ ; \qquad \text{with} \quad K_\beta, \ a_0 = \frac{1.389 \times 10^{-8}}{2 \times 0.0833} = 8.345 \ \text{Å}.$$

the mean value being 8.256 Å.

DISCUSSION

As in the case with NaCl, the spacing of KCl dissolved in B$_2$O$_3$ glass is found to be larger than in the normal salt, the extent of enlargement being about 36%, considerably

less than the corresponding value in the former case. Also the spacing is found to be independent of the KCl concentration.

It is well known, however, that slight changes of lattice distance are observed in the case of alloys in which a metallic atom displaces another from its position in the lattice producing a certain deformation of the units. But the change in such cases is never beyond a small percentage which is quite small compared with the large change observed by us. Experiments carried out by Randall, Rooksby and Cooper (Z. Krist., 1930, 75, 196) on various glasses brought out the idea that the lattice constants of a crystal do not remain constant as the crystalline particles vary in size. Experiments on the so-called ' amorphous ' carbon by Lowry and Bozerth (J. Phys. Chem., 1928, 32, 1524) and by Randall and Rooksby (Nature, 1932, 129, 280) and Hofmann (Ber., 1926, 59, 2433) also suggest the same conclusion. Lennard Jones (Z. Krist., 1930, 75, 215) has given theoretical reasons for anticipating the results. He has calculated that for small crystals consisting of 500 units, the spacing is 5% greater than in the ordinary crystal. For crystals of five layers thick each way, the change calculated is 7% and for minute crystals consisting of 3 units each way it is 14%. In no case, however, the expansion of the lattice caused evidently by the modification of the mutual polarising forces, is greater than 10—15% and is therefore inadequate to explain the very large expansion suffered by the lattice. The reason therefore has to be sought for elsewhere.

The possibility of the formation of less known and comparatively unstable borates in the glass is not excluded. But even if the borates like $5B_2O_3$, K_2O be formed, they are present *in such small quantities* that they would not give any pronounced diffraction lines. It has been found that a concentration of these salts in glass less than 5-10% will not give any diffraction pattern at all. Whether crystalline anhydrous boric oxide has been formed also requires explanation. It is unlikely that B_2O_3-glass, which normally does not give any diffraction lines, should show strong devitrification when a salt like KCl is dissolved in it. Moreover, a similar system containing dissolved NaCl instead of KCl (Majumdar, & Palit, loc. cit.) did not show the same lines, which would have been the case if the extra lines were due to devitrified B_2O_3. The matter is under further investigation.

About the weak lines with KBO_2 it may be said that the same exposure (of about 12 hours) was given in each case including that of the borate. The weakness of the lines is not therefore due to smaller exposure but to greater absorption of X'rays by the salt.

A tentative explanation of the phenomenon is suggested below. When a crystal is made to dissolve in a glass melt and the latter allowed to solidify, very much the same type of forces will operate as if the crystal were present in a solution of lesser viscosity, like water, with the difference that the magnitude of some of the forces will be altered. On account of the altered dielectric, there will be a shielding of the electrostatic forces, bringing about a general weakening in their magnitude. The dielectric constant of the medium employed is about 3.5 (Thomas, J. Phys. Chem., 1931, 35, 2109). It is natural to expect that the short distance repulsive forces will also be weakened to a certain extent by the shielding action of the altered dielectric, but these will not be probably weakened to the same extent as the purely electrostatic forces. Hence when the ions of the crystal take up their equilibrium positions in the lattice, they are shifted to a greater distance than would be the case if the crystalisation had taken place from the melt of the pure crystal

or from its aqueous solution. It may be added, however, that the dielectric constant is a macroscopic and not a microscopic term, representing as it does in some way or other, the total effect of the shielding which is produced on the component ions. Hence the explanation attempted must be regarded more or less qualitative, until it can be proved experimentally that the spacnigs of the same crystal dissolved in two glass media vary inversely as their dielectric constants.

The fact that concentration of KCl (7.2%, 7.8%, 8.13%) has practically no influence on the dimension of the space lattice also needs explanation. It is apparent that in the new space lattice of the alkali halide, its own concentration has no effect on the various forces within the system. It is believed by Warren, Zachariasen and others that in alkali borate glass, the alkali ions are situated within the hollows of the *non-periodic* network formed by the boron-oxygen-boron groupings. The alkali halide lattice in a glass of boron trioxide may therefore be supposed to be formed within the hollows of the network, the only effect on the alkali and the halogen ions being the shielding action produced by the immediate environment, which in this case consists of boron and oxygen atoms joined by purely co-valent linkages. The concentration of the alkali halide itself in such a scheme will have no effect on the arrangement of its own lattice. It will only modify the relative density of the salt within the glass. Most likely its distribution within the glass is not what we usually take to be homogeneous.

It has been noticed by Majumdar and Sarma (*J. Indian Chem. Soc.*, 1942, **19**, 241) that alkali halides dissolved in boric oxide glass show the same deformation effect as would be required by Fajans' theory of deformation (Fajans and Joos, *Z. Physik*, 1923, **23**, 1) with the modification that in the case of chlorides containing small cations like LiCl, the amount of deformation produced is very much greater than in corresponding aqueous solutions of the crystal. It has also been found that the amount of deformation produced progressively decreases with the increase in diameter of the cation. Thus in the system CsCl—B_2O_3, there is practically no change in the mol-refraction values from those of the crystals and dilute solution. It should be stated here that the results of X'ray analysis of the two cases, NaCl and KCl dissolved in B_2O_3 glass apparently indicate a change in the opposite sense. For, while in the case of NaCl, the increase in spacing amounts to 60%, in the case of KCl it is only 36%. Normally we can expect a stronger deformation in the case of NaCl.

Experiments are in progress to measure the spacing of RbCl and CsCl dissolved in the same medium.

Our thanks are due to the Late Prof. B. B. Ray, Khaira Professor of Physics, University of Calcutta, in whose laboratory the X'ray photographs were taken.

THE EFFECT OF NEUTRAL SALTS ON THE HYDROLYSIS OF MAGNESIUM SULPHATE

BY BALWANT SINGH AND AHSANULHAQ REHMANN

The hydrolysis and the effect on the hydrolysis of magnesium sulphate in aqueous solution, by the neutral salts—sodium chloride, sodium iodide and potassium iodide have been studied potentiometrically at 25°, using quinhydrone electrode coupled with saturated calomel electrode.

The hydrolysis, as also the effect of neutral salts on the hydrolysis of different substances, in aqueous solutions, have been studied by various workers. O'Sullivan (*Trans. Faraday Soc.*, 1925, **21**, 319) used the quinhydrone electrode in the measurement of p_H values in solutions containing magnesium and other bivalent ions of metals namely copper, zinc, nickel, cobalt, iron and cadmium, in their sulphate solutions. He did not study the effect of neutral salts on the hydrolysis of these salts.

Poma and Albonico (*Atti Accad. Lincei*, 1915, **24**, I, 747) found that neutral salts accelerated the rate and increased the degree of hydrolysis of methyl acetate.

The hydrolysis of salts of beryllium and aluminium, derived from strong acids has been investigated by Cupr (*Publ. Fac. Sci. Univ. Masaryk*, 1931, **133**, 3) using the quinhydrone electrode. The influence of neutral salts on the hydrolysis of beryllium chloride and beryllium bromide was ascribed to hydration.

Friedman and Stokes (*J. Amer. Chem. Soc.*, 1939, **61**, 118) employed an electrometric method, using quinhydrone electrode coupled with a calomel electrode, to determine the effect of neutral salts on the hydrolysis of copper sulphate in aqueous solution. They found that potassium nitrate, potassium chloride and sodium chloride increased the degree of hydrolysis of copper sulphate solution in the given order. Those which showed a decrease are in the order of sodium sulphate and potassium sulphate.

In the present investigation the quinhydrone electrode has been employed to determine the effect of sodium chloride, sodium iodide and potassium iodide on the hydrolysis of magnesium sulphate ($MgSO_4$, $7H_2O$) in aqueous solution.

EXPERIMENTAL

All salts used in this investigation were 'Analar' (B.D.H.) quality. In all operations freshly boiled distilled water was used.

The quinhydrone electrode (a piece of bright platinum foil dipping into the salt solution in which sufficient quantity of solid 'Analar' quinhydrone has been added to make the solution saturated at 25°) was coupled with a saturated calomel electrode, the liquid junction potentials being eliminated by using a sturated potassium chloride—agar-agar bridge for coupling the electrodes. The set-up was placed in a water-bath, the temperature of which was maintained at 25° by an electromagnetic relay in conjunction

with a thermo-regulator. It was allowed to attain the temperature of the thermostat before measurements were made. The measurements were repeated over intervals of two to five minutes, for a period of ten to twenty minutes, depending upon the constancy of the readings.

From the E.M.F. the p_H and then the hydrogen-ion concentration of the solution was calculated.

From the hydrogen-ion concentration of the solution, its degree of hydrolysis (x) was calculated from the formula $x=(H)/2M$ where (H) is the concentration of hydrogen ions in the solution resulting from the hydrolysis of the salt, and M is the molar concentration of the salt.

In the following tables, (V) denotes the molar dilution and E.M.F., the measured electromotive force in salts; (H) is the hydrogen-ion concentration in g. mols. per litre and $100x$ is the %hydrolysis calculated.

<div align="center">

TABLE I

Magnesium sulphate

Added salt : None.

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Dilution (V).	E.M.F.		p_H.	[H]$\times 10^5$.	%Hydrolysis ($100x$).
10	0.1570 volts				
	0.1570				
	0.1580				
20	0.1680	Av : 0.1575	4.869	1.352	0.0068
	0.1680				
	0.1680				
40	0.1760	Av : 0.1680	4.670	2.138	0.0214
	0.1770				
	0.1770				
80	0.1840	Av : 0.1767	4.523	2.999	0.0600
	0.1840				
	0.1830				
100	0.1880	Av : 0.1837	4.404	3.945	0.1578
	0.1890				
	0.1890				
320	0.1920	Av : 0.1887	4.319	4.797	0.3838
	0.1920				
	0.1930				
640	0.1950	Av : 0.1923	4.258	5.521	0.8834
	0.1960				
	0.1950				
1280	0.1980	Av : 0.1953	4.209	6.180	1.9776
	0.1980				
	0.1970				
		Av : 0.1977	4.168	6.792	4.3469

TABLE II
Magnesium sulphate
Added salt. : 0.25M-NaCl.

Dilution (V).	E.M.F.		p_{H}.	[H] $\times 10^5$.	%Hydrolysis (100x).
10	0.1600 volts				
	0.1600				
	0.1590				
		Av : 0.1597	4.811	1.545	0.0077
20	0.1710				
	0.1720				
	0.1720				
		Av : 0.1717	4.607	2.472	0.0247
40	0.1810				
	0.1810				
	0.1810				
		Av : 0.1810	4.450	3.548	0.0709
80	0.1860				
	0.1870				
	0.1870				
		Av : 0.1867	4.353	4.436	0.1774
160	0.1910				
	0.1910				
	0.1910				
		Av : 0.1910	4.281	5.236	0.4189
320	0.1950				
	0.1940				
	0.1940				
		Av : 0.1943	4.225	5.957	0.9531
640	0.1970				
	0.1960				
	0.1970				
		Av : 0.1967	4.184	6.546	2.0947
1280	0.1990				
	0.1990				
	0.1980				
		Av : 0.1987	4.151	7.063	4.5203

TABLE III
Magnesium sulphate
Added salt : 0.25M-NaI.

Dilution (V).	E.M.F.		p_{H} .	[H]$\times 10^5$.	%Hydrolysis (100x).
10	0.1100				
	0.1100				
	0.1100				
		Av : 0.1100	5.651	0.2234	0.0011
20	0.1180				
	0.1180				
	0.1190				
		Av : 0.1183	5.510	0.3090	0.0031
40	0.1250				
	0.1250				
	0.1250				
		Av : 0.1250	5.397	0.4009	0.0080
80	0.1310				
	0.1310				
	0.1320				
		Av : 0.1313	5.291	0.5117	0.0205
160	0.1370				
	0.1370				
	0.1380				
		Av : 0.1373	5.189	0.6471	0.0518
320	0.1430				
	0.1430				
	0.1430				
		Av : 0.1430	5.093	0.8073	0.1292
640	0.1470				
	0.1470				
	0.1480				
		Av : 0.1473	5.002	0.9954	0.3185
1280	0.1460				
	0.1470				
	0.1470				
		Av : 0.1467	5.030	0.9333	0.6873

Varying amounts (0.25M, 0.50M, 0.75M, 1.00M and 1.50M) of sodium chloride, sodium iodide and potassium iodide were added to magnesium sulphate solution and their effect on the hydrolysis of the solution was studied. The results have been shown in Tables IV, V and VI.

TABLE IV

Magnesium sulphate

Molality of added NaCl

	0.50M		0.75M		1.00M		1.50M	
Dilution.	Av. E.M.F.	(100x).	Av. E.M.F.	(100x).	Av. E.M.F.	(100x).	Av. E.M.F.	(100x).
10	0.1653	0.0096	0.1697	0.0114	0.1743	0.0137	0.1837	0.0197
20	0.1760	0.0292	0.1803	0.0345	0.1833	0.0388	0.1937	0.0582
40	0.1853	0.0840	0.1883	0.0944	0.1927	0.1120	0.1997	0.1472
80	0.1887	0.1919	0.1917	0.2203	0.1973	0.2680	0.2030	0.3358
160	0.1925	0.4406	0.1947	0.4842	0.1993	0.5795	0.2047	0.7146
320	0.1957	1.0050	0.1977	1.0893	0.2010	1.2364	0.2060	1.5036
640	0.1983	2.2240	0.1997	2.3558	0.2023	2.6070	0.2070	3.1270
1280	0.1997	4.7117	0.2010	4.9453	0.2027	5.2995	0.2077	6.4320

TABLE V

Magnesium sulphate

Molality of added NaI

	0.50M		0.75M		1.00M		1.50M	
Dilution.	Av. E.M.F.	(100x).	Av. E.M.F.	(100x).	Av. E.M.F.	(100x).	Av. E.M.F.	(100x).
10	0.1030	0.0009	0.0867	0.0005	0.0803	0.0004	0.0590	0.0002
20	0.1087	0.0021	0.0900	0.0010	0.0820	0.0008	0.0620	0.0003
40	0.1133	0.0051	0.0930	0.0023	0.0837	0.0016	0.0643	0.0008
80	0.1177	0.0121	0.0953	0.0050	0.0850	0.0034	0.0660	0.0016
160	0.1213	0.0277	0.0970	0.0108	0.0863	0.0071	0.0670	0.0033
320	0.1240	0.0617	0.0983	0.0227	0.0870	0.0146	0.0677	0.0068
640	0.1253	0.1298	0.0993	0.0470	0.0873	0.0295	0.0683	0.0141
1280	0.1237	0.2439	0.0983	0.0906	0.0867	0.0574	0.0673	0.0271

TABLE VI

Magnesium sulphate

Molality of added KI

Dilu-tion.	0.25M		0.50M		0.75M		1.00M		1.50M	
	Av. E.M.F.	(100x).	Av. E.M.F.	(100x).	Av. E.M.F.	(100x).	Av. E.M.F.	(100x).	Av. E.M.F.	(100x)
10	0.0897	0.0005	0.0777	0.0003	0.0637	0.0002	0.0460	0.0001	0.0233	0.00009
20	0.0947	0.0012	0.0793	0.0007	0.0643	0.0004	0.0470	0.0002	0.0240	0.00008
40	0.0970	0.0027	0.0800	0.0014	0.0647	0.0008	0.0480	0.0004	0.0243	0.00016
80	0.0987	0.0057	0.0803	0.0028	0.0650	0.0020	0.0483	0.0008	0.0247	0.00032
160	0.1000	0.0121	0.0800	0.0056	0.0653	0.0031	0.0487	0.0016	0.0250	0.00065
320	0.1007	0.0248	0.0790	0.0107	0.0653	0.0063	0.0483	0.0064	0.0253	0.00132
640	0.1003	0.0490	0.0783	0.0208	0.0640	0.0109	0.0480	0.0064	0.0253	0.00269
1280	0.0987	0.0918	0.0777	0.0405	0.0613	0.0214	0.0473	0.0124	0.0250	0.00520

FIG. 1

FIG. 2

FIG. 3

It is evident that the hydrolysis of magnesium sulphate in aqueous solution increases with dilution and is further enhanced on the addition of sodium chloride. But, it is suppressed by the addition of sodium iodide and potassium iodide, in the given order; the decrease being more and more marked with the increase in concentration of the added salt.

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ON THE HYDROLYSIS OF CANESUGAR IN PRESENCE OF ACID SOL

By T. Banerjee and B. Bhatta

The study of the influence of acid sols on the velocity of hydrolysis of canesugar has revealed that we are here dealing with a simultaneous reaction, (a) the inversion of canesugar in the homogeneous liquid phase by H$^+$ ions present in that phase, and (b) the inversion taking place on the surface of the acid sols. The velocity of this second reaction is proportional to the concentration of the acid sol.

This investigation has been undertaken to study the influence of acid sols on hydrolysis of canesugar.

Experimental

The course of inversion of sucrose whether by hydrochloric acid alone, or in presence of colloidal acids, has been followed by means of a polarimeter of Schmidt and Haensch type. The observation tube was surrounded water-tight by a metallic box, covered all over with asbestos board. Since the tungstic acid sol was found to be reduced when it came in contact with any metal, specially copper, zinc, tin, nickel, antimony, the observation tube was made of glass with circular plane parallel plates of glass, pressed water-tight against the polished ends of the tube by means of screw-caps. The length of the tube used is 1 dcm. The temperature of the box surrounding the observation tube was kept constant within 0.1° throughout the experiment by circulating water by means of a pump from an electrically heated thermostat. The source of light used is a sodium lamp supplied by Zeiss which is made spectroscopically homogeneous by passing it through a potassium dichromate filter.

All the chemicals used in the present investigation were of high grade of purity, either Merck's or Kahlbaum's reagents.

A mixture of x c.c. of sodium tungstate of definite strength (say 0.1 M) and x c.c. of HCl of definite strength (say 0.2N), kept for sometime to ensure the formation of sol, was mixed with 2x c.c. of sucrose solution of definite strength (say 20% solution). The p_H of this mixture was then determined by using a quinhydrone electrode; the hydrogen electrode could not be used, as it has been found that the tungstic acid sol is reduced by hydrogen gas. The solution of hydrochloric acid (2x c.c.), which together with 2x c.c. of the same sugar solution will give exactly the same p_H as the above mixture (of HCl, sucrose and colloidal acid), was prepared by repeated trial.

The observation tube (rather the box surrounding it) was kept in place and the box was raised to the desired temperature by passing water from the thermostat, the circulation of water having been so satisfactorily regulated that the temperature remained constant within 0.1°. The circulation was stopped for a minute and the observation tube was quickly filled with the reaction mixture. The temperature of the reaction mixture was raised to that of the bath before it was introduced into the observation tube. The water was circulated again and when the temperature became constant, polarimetric readings were taken at intervals. The final reading was taken after passing water at a still higher temperature for some hours to ensure complete reaction and then maintaining the system at the temperature at which the reaction had been studied until they became constant.

The unimolecular velocity constant was calculated according to the equation:

$$k = 2.3/t_n \cdot \log_{10}(A_0 - A) - \log_{10}(A_n - A) \qquad \ldots \ (1)$$

where A_0 = the initial angle of rotation,

           A_n = the angle of rotation at the time n,

           A = the final angle of rotation, and

           t_n = time which has elapsed since the reaction started.

The hydrolysis experiments had to be carried out at 60° and 70° as otherwise for the p_n of the system used (between 2 and 3), the velocity becomes too small to be measured within reasonable time intervals.

TABLE I

Influence of p_n on hydrolysis of 10% sucrose solution.

	(a) with HCl at 70°.			(b) with HCl+0.25M tungstic acid at 70°.		
p_n at 30° ...	2.05	2.42	2.99	2.05	2.42	2.99
k_1 at 70° ...	0.0172	.00635	0.00164	0.02023	0.00837	0.00245

TABLE II

Influence NaCl on hydrolysis of 5% sucrose solution.

				Conc. of NaCl	
				0	0.43 M
p_n at 30°	...	...	...	2.42 M	2.42
k_1 at 70°	...	...	...	0.00632	0.00635

The salt effect due to the presence of sodium chloride when tungstic acid sol is formed by the addition of hydrochloric acid to the sodium tungstate has been found to be negligible for a salt concentration of 0.038M (the amount formed from 0.025M sodium tungstate, according to the equation $4Na_2WO_4 + 6HCl \rightleftharpoons Na_2O, 4WO_3 + 6NaCl + 3H_2O$) as will be seen from the table.

TABLE III

Influence of tungstic acid sol upon hydrolysis of 10% sucrose solution at 70°.

p_n at 30°.	k_1 with HCl (comp. as in Table Ia).	k_1 with tungstic acid (comp. as in Table Ib)	% Diff.
2.05	0.01720	0.02023	14.9
2.42	0.00635	0.00837	24.1
2.99	0.00164	0.00245	33.0

It is obvious from Table III that the presence of tungstic acid sol appreciably enhances the velocity of hydrolysis and the relative enhancement becomes greater, the greater the p_n of the system, other factors remaining the same.

The p_n of the reaction mixture remained constant throughout the experiments, 8 hours being the maximum time taken. The p_n also did not change on heat treatment of the solution to a temperature of 70° and cooling again to 30°.

<div align="center">TABLE IV</div>

p_H at 30°.	Temp.	(a) With HCl		(b) With HCl and 0.025M tungs-state.	
		k_1.	$\dfrac{k_{(t°+10°)}}{k_t}$.	k_1.	$\dfrac{k_{(t°+10°)}}{k_t}$.
(a) 2.05	60°	0.00634	2.73	0.00742	2.73
2.05	70	0.01720		0.02023	
(b) 2.42	60	0.00238	2.65	0.00304	2.75
2.42	70	0.00635		0.00837	

It will be seen that the temperature coefficient of the velocity constant of hydrolysis is the same in hydrochloric acid solution or in tungstic acid sol andhydorchloric acid mixture.

<div align="center">TABLE V</div>

<div align="center">*Influence of tungstic acid conc.*</div>

<div align="center">Temp. = 30. p_H = 2.42. - Conc. of sucrose = 5%.</div>

Tungstate conc. (M)	...	..	0.25	0.05	0.075
k_1 at 30°	...	...	0.00800	0.00951	0.01081

<div align="center">TABLE VI</div>

<div align="center">*Influence of silicic acid on hydrolysis.*</div>

<div align="center">Temp. = 70°.   Conc. of Na silicate = 0.1M.   Conc. of HCl = 0.165M,
p_H at 30° = 2 05</div>

Conc. of sucrose.	k_1 with HCl (alone).	k_1 with HCl & silicic acid mixture.	%Diff.
10M	0.00489	0.00611	19.9
20	0.00519	0.00643	19.3

As the sol concentration increases, the velocity constant of hydrolysis increases. Fig. 1 shows that if the value of k_1 is obtained by extrapolation for zero concentration of tungstic acid sol, we get the value 0.00640 which is practically the velocity constant observed (0.00635) with pure hydrochloric acid at p_H 2.42.

<div align="center">FIG. 1</div>

Conc of tungstate (M).

It is thus clear that we are dealing with two independent velocities, one due to hydrochloric acid in homogeneous solution of p_H 2.42 and the other due to the presence of tungstic acid sol particles in the medium. The surface area of the sol particle may be considered to be proportional to the concentration of the sol, if the particles are of uniform size and the increased velocity must be ascribed to the hydrolysis of canesugar on the surface of the sol. Thus we have,

$$dx/dt=dc_0/dt+dc_1/dt$$

where dx/dt is the observed change.

dc_0/dt is the change due to H^+ in the homogeneous solution and dc_1/dt is the change due to the reaction on the surface of tungstic acid sol.

Again

$$dc_1/dt=k_1.Sp_H.C$$

or

$$-1/C.dc/dt=k_1Sp_H$$

where $S=$surface of tungstic acid sol and $C=$conc. of sucrose.

The observed unimolecular velocity constant minus the velocity constant due to hydrolysis by HCl alone for the same p_H^2 should therefore be proportional to the concentration of tungstic acid sol in the medium, which is actually found to be the case.

DISCUSSION

Weigner (*J. Soc. Chem. Ind.*, 1931, **50**, 110T) has compared the concentrations of hydrogen ions in suspensions of acid clay, tungsten trioxide (aged), silica, etc. potentiometrically and inversometrically. With suspensions of tungsten oxide (aged) and silica, he reported the following data :—

				$\dfrac{C_H^+ \text{ inversometrically}}{C_H^+ \text{ potentiometrically}} \times 100.$
Uncoagulated suspensions	..	..	..	
Silica	..	..	..	.. 115.5
Tungsten oxide (aged) coagulated suspension	..	114.5
Silica	..	..	..	.. 1.47

He pointed out that the differences in the above ratio observed with uncoagulated suspension of tungsten oxide and silica were not great. Our experiments have shown that the difference observed by Weigner with suspensions of tungsten oxide and silica, though not great, was definite and have quantitatively corroborated the findings of Weigner.

It has also been shown that we are here dealing with a simultaneous chemical reaction, (a) the inversion of canesugar in the homogeneous liquid phase by the H^+ ions present in that phase, and (b) the inversion taking place on the surface of the sol particles due to the influence of the H^+ ions attached to that surface on the canesugar molecules which have diffused into that surface. The velocity of this second reaction is proportional to the concentration of tungstic acid sol.

ON THE PREPARATION OF SULPHANILAMIDE DERIVATIVES. PART I. SULPHANILYL CYANAMIDE
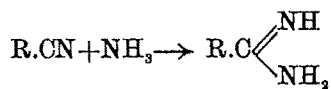
BY P. K. DAS-GUPTA AND P. GUPTA

A method has been described by which sulphanilyl cyanamide may be prepared by the action of an alkyl sulphocyanide on an alkali salt of p-aminobenzene sulphonamide.
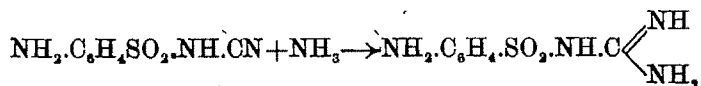
Certain sulphanilamido derivatives like sulphaguanidine, sulphathiazole, sulphadiazine etc. are being found to be specific antibacterial therapeutic agents. As such, it was considered to be of interest to search for methods by which compounds of this nature can be synthesised.

On consulting the literature, it was noticed that one of the methods of preparing sulphaguanidine is by heating p-aminobenzene sulphonamide with dicyandiamide (Buttle, $et\ al.$, $Biochem.\ J.$, 1938, 32, 1101). Later on it was prepared by the action of ammonium nitrate on the calcium salt of acetyl sulphanilylcyanamide at a high temperature (Indian Patent, No. 29542) and subsequent hydrolysis.
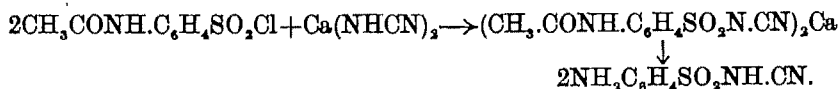
It is well known that cyanide reacts with ammonium salts to give an amidine

$$R.CN + NH_3 \longrightarrow R.C \begin{array}{l} \diagup NH \\ \diagdown NH_2 \end{array}$$

It is quite natural to expect that p-aminobenzene sulphoncyanamide itself might react with ammonia-yielding substance to form sulphaguanidine as follows :—
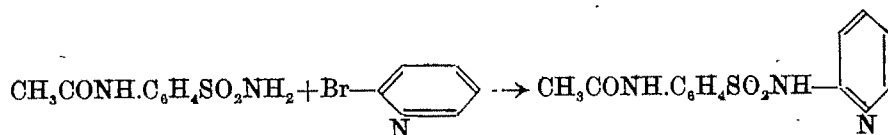
$$NH_2.C_6H_4SO_2.NH.CN + NH_3 \longrightarrow NH_2.C_6H_4.SO_2.NH.C \begin{array}{l} \diagup NH \\ \diagdown NH_2 \end{array}$$

Sulphanilyl cyanamide was first prepared by Winnek $et\ al$ ($J.\ Amer.\ Chem.\ Soc.$, 1942, 64, 1682) by reacting acetaminobenzene sulphonyl chloride with calcium cyanamide and subsequent hydrolysis.

$$2CH_3CONH.C_6H_4SO_2Cl + Ca(NHCN)_2 \longrightarrow (CH_3.CONH.C_6H_4SO_2.N.CN)_2Ca$$
$$\downarrow$$
$$2NH_2C_6H_4SO_2NH.CN.$$

But no direct synthesis from sulphanilamide itself has up till now been attempted.

It is known that the amide hydrogen of sulphanilamide is replaceable either by sodium or by halogen ($cf.$ Roy, $J.\ Proc.\ Inst.\ Chemist$, 1944, 16, 76). It is also known that the sodium salt of acetyl sulphanilamide reacts with bromopyridine to give acetyl sulphanilylpyridine (Indian Patent, No.27477).

$$CH_3CONH.C_6H_4SO_2NH_2 + Br \underbrace{\diagup \diagdown}_{N} \dashrightarrow CH_3CONH.C_6H_4SO_2NH \underbrace{\diagup \diagdown}_{N}$$

So it was thought possible to obtain sulphanilyl cyanamide either by reacting the sodium salt of acetyl sulphanilamide with cyanogen bromide or by reacting acetaminobenzene

sulphon-sodio (or potassio) chloro (or bromo) amide (Todd, Fletcher, *et al.*, *J. Amer. Chem. Soc.*, 1943, **65**, 350) with sodium or potassium cyanide and subsequent hydrolysis according to the following schemes respectively.

$$CH_3CONH.C_6H_4SO_2NH.Na$$
$$\downarrow CNBr$$
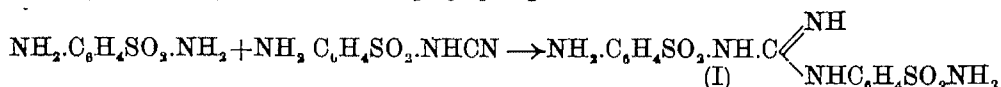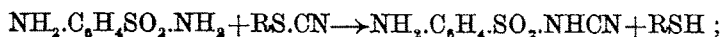$$CH_3CONH.C_6H_4SO_2NH.CN \longrightarrow NH_2C_6H_4SO_2NHCN.$$
$$\uparrow NaCN$$
$$CH_3CONH.C_6H_4SO_2NHBr$$

But by varying the reactants, or changing the mode of reactions in divergent ways, no such reaction could be brought about in any appreciable yield. Reacting alkyl sulpho-cyanide with an alkali metal salt of sulphanilamide, however, in pressence of a phenolic solvent, the reaction proceeded as follows :—

$$NH_2.C_6H_4SO_2.NH_2 + RS.CN \longrightarrow NH_2.C_6H_4.SO_2.NHCN + RSH ;$$

$$NH_2.C_6H_4SO_2.NH_2 + NH_2 C_6H_4SO_2.NHCN \longrightarrow NH_2.C_6H_4SO_2.NH.C \overset{NH}{\underset{NHC_6H_4SO_2NH_2}{\diagdown}}$$
$$(I)$$

The sulphanilyl (*p*-sulphonamidophenyl) guanidine (I), which is partly formed during the course of the reaction by the interaction of the sulphanilyl cyanamide formed, with unchanged sulphanilamide, can be easily separated out from the reaction mixture by partial acidification. The mother-liquor on complete acidification readily affords sulphanilyl cyanamide which crystallises from water in clusters of needles, m.p. 292°.

EXPERIMENTAL

Attempts to Synthesise p-Aminobenzene-sulphoncyanamide

Sulphanilamide, as available in the market, was purified by crystallisation from water and the product melting at 164-66° was used throughout the course of the investigation.

p-Acetaminobenzene sulphonamide (5 g.), sodium bicarbonate (4g.) and water (50 c.c.) were mixed in a 100 c.c. conical flask. To this cyanogen bromide (3g.) was added and the whole thing shaken for 8 hours and left overnight at the room temperature. Next day it was filtered and washed with water. The residue melted at 215° and showed no depression in melting point when mixed with an authentic sample of *p*-acetaminobenzene sulphonamide. The filtrate on acidification yielded a white crystalline substance, which was also found to be *p*-acetaminobenzene sulphonamide. Similarly, no condensation was brought about by reacting *p*-acetaminobenzene sulphonamide with cyanogen bromide in boiling acetone, by refluxing with xylene in presence of potassium carbonate and copper bronze, nor in a sealed tube at 125-130° for 3 hours. Even the sodium salt of *p*-acetaminobenzene sulphonamide failed to react with cyanogen bromide when refluxed for 4 hours in alcoholic suspension.

p-Acetaminobenzene sulphon-sodio (or potassio) chloro (or bromo) amide, prepared according to the method of Todd *et al.* could not also be condensed with sodium or potassium cyanide in aqueous, alcoholic or in any neutral solvent by any of the procedures as mentioned above.

Condensation of p-Aminobenzene-sulphonamide with Alkyl Sulphocyanide

Preparation of Sulphanilyl Cyanamide.—Sodium salt of *p*-aminobenzene sulphonamide (9 parts) was taken in phenol (18 parts) and the mixture heated to 150°, ethyl sulphocyanide (4 parts) was gradually added to the mixture during the course of an hour. After that the whole thing was heated for 2 hours at 180°. The reaction mixture was then cooled and diluted with benzene when a solid separated out. This was dissolved in water and the solution partially neutralised with 2 c.c. of concentrated hydrochloric acid when a solid again separated out (A). The mother-liquor was again neutralised with 2.6 c.c. of concentrated hydrochloric acid under ice-cooling. Crystals, m.p. 280-85°, thus obtained were further purified by recrystallisation from water (charcoal) as needles, m.p. 292°. (Found : N, 21.5 ; S, 16.2. $C_7H_7O_2N_3S$ requires N, 21.3 ; S, 16.3 per cent).

The sodium salt of *p*-aminobenzene sulphonamide (10.7 parts) in phenol (21 parts) was heated to 150° and methyl sulphocyanide (4 parts) gradually added to the mixture and the heating continued for 1 hour at 180°. The reaction mixture was cooled and diluted with benzene, filtered and a solid separated from which *p*-aminobenzene sulphoncyanamide, m.p. 292° is obtained in the same way as above.

To sodium salt of *p*-aminobenzene sulphonamide (10.7 parts) taken in 21 parts of cresol and heated to 150° methyl sulphocyanide (4 parts) was gradually added and the heating continued for 1 hour more at 180°. The reaction mixture was treated as in the previous examples and *p*-aminobenzene sulphoncyanamide, m.p. 292° obtained as in the previous cases.

The paper is based on a pending patent application.

In conclusion the authors wish to express their sincere thanks to Dr. U. P. Basu, D.Sc., for his interest in the course of these investigations.

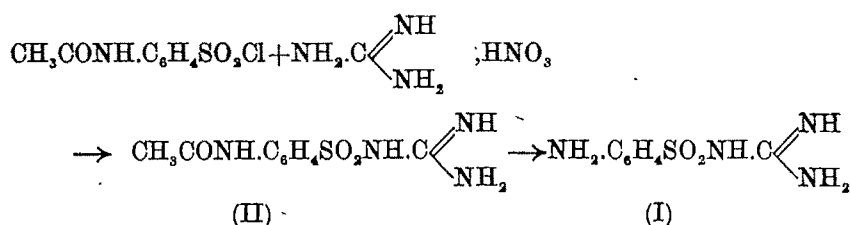BENGAL IMMUNITY RESEARCH LABORATORY,
    CALCUTTA.

ON THE PREPARATION OF SULPHANILAMIDE DERIVATIVES. PART II. SULPHANILYLGUANIDINE
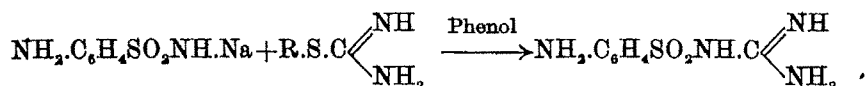
By P. K. Das-Gupta and P. Gupta

A method has been described by which sulphanilylguanidine may be prepared by the action of ammonia on sulphanilyl cyanamide.
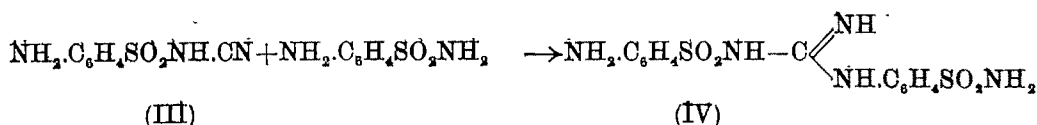
Sulphanilylguanidine (I) is considered to be a valuable antibacterial agent, particularly in the treatment of bacillary dysentery. It was first prepared by Buttle *et al* (*Biochem. J.*, 1938, **32**, 1101) by heating p-aminobenzene sulphonamide with dicyandiamide. Subsequently, it has been prepared by the action of guanidine nitrate on acetyl sulphonyl chloride in acetone and subsequent hydrolysis of the reaction product (*cf.* I.P., 28363) :

$$CH_3CONH.C_6H_4SO_2Cl + NH_2.C{\Big\langle}^{NH}_{NH_2}\quad ;HNO_3$$

$$\rightarrow CH_3CONH.C_6H_4SO_2NH.C{\Big\langle}^{NH}_{NH_2} \rightarrow NH_2.C_6H_4SO_2NH.C{\Big\langle}^{NH}_{NH_2}$$

$$(II) \qquad\qquad\qquad\qquad (I)$$

The same acetyl sulphonyl chloride (II) reacts with *iso*thiourea and the resulting condensation product on treatment with ammonia or any salt that liberates ammonia on heating, affords the acetylsulphanilylguanidine. (II). This latter compound as usual undergoes hydrolysis to sulphaguanidine (*vide* I.P., 29526). It has been subsequently noticed (I.P. 29613) that the *iso*thiourea can be condensed with sodium salt of sulphanilamide in presence of phenol to give rise directly to sulphanilylguanidine.

$$NH_2.C_6H_4SO_2NH.Na + R.S.C{\Big\langle}^{NH}_{NH_2} \xrightarrow{\text{Phenol}} NH_2.C_6H_4SO_2NH.C{\Big\langle}^{NH}_{NH_2}\ ,$$

While reacting the sodium salt of p-aminobenzene sulphonamide with alkyl sulphocyanides in phenolic medium to produce o-aminobenzene sulphonocyanamide (III) (*cf.* Part I of the series), a guanidine derivative—sulphanilyl (p-sulphonamidophenyl) guanidine (IV), m.p. 216° shown in the experimental portion of the present paper, was isolated. The reaction proceeds as follows :

$$NH_2.C_6H_4SO_2NH.CN + NH_2.C_6H_4SO_2NH_2 \rightarrow NH_2.C_6H_4SO_2NH-C{\Big\langle}^{NH}_{NH.C_6H_4SO_2NH_2}$$

$$(III) \qquad\qquad\qquad\qquad (IV)$$

The formation of the above complex guanidine derivative (IV) by the interaction of the amino grouping of unreacted sulphanilamide with the cyano group of sulphanilyl cyanamide (III) indicated that the latter could readily undergo condensation with any

amine or ammoniacal bodies. This expectation has been fully realised by isolating sulphanilylguanidine itself from the above sulphanilyl cyanamide under the experimental conditions as described in this paper.

EXPERIMENTAL

Preaparation of Sulphanilylguanidine

(i) A mixture of the sodium salt of p-aminobenzene sulphoncyanamide, m.p. 292° (7 parts), 7 parts of phenol and dry ammonium nitrate (2.5 parts) was heated at 180° for 1 hour. The mixture was diluted with benzene and the solid separating was collected and washed with dilute alkali. A solid that was left behind was crystallised from water in clusters of needles, m.p. 189°, after being dried at 100°. Mixed m.p. with an authentic sample of sulphaguanidine showed no lowering. Solubility in water=250 mg. per 100 c.c., p_{π} of the solution so obtained=6.9, solubility in alcohol=600 mg. per 100 c.c. It forms hydrochloride, m.p. 205°. (Found : N, 26.25. $C_7H_{10}O_2N_4S$ requires N, 26.16 per cent).

(ii) A mixture of the sodium salt of p-aminobenzenes ulphoncyanamide, cresylic acid (7 parts) and dry ammonium nitrate (2.5 parts) was heated at 180° for 1 hour. By following the method as in (i), p-aminobenzene sulphonylguanidine was obtained as usual.

(iii) A stream of dry ammonia was passed while a mixture of the sodium salt of p-aminobenzene sulphoncyanamide (7 parts) and 7 parts of phenol was being gradually heated to 180°. The heating and passing of ammonia were continued for 1 hour at this temperature. The mixture was cooled and diluted with benzene. The solid was treated as in (i) and p-aminobenzene sulphonylguanidine was obtained.

(iv) p-Aminobenzène sulphonylguanidine was also obtained exactly in the same manner as in (iii) by using cresol instead of phenol as a solvent.

(v) The sodium salt of p-nitrobenzene sulphonamide (22.4 parts) was heated with 45 parts of phenol to 150°. To it was added ethyl sulphocyanide (8.7 parts) gradually with stirring. After 1 hour ammonium nitrate (8 parts) was added and the heating continued for 1 hour more at 180°. This was cooled and diluted with benzene. The solid that was obtained, was treated as in (i) when p-nitrobenzene sulphonylguanidine, m.p. 214° (with decomposition) was isolated. (Found : N, 23.1. $C_7H_8O_4N_4S$ requires N, 22.95 per cent). This nitro compound was reduced with iron and hydrochloric acid in the customary way and p-aminobenzene sulphonylguanidine isolated from the reaction mixture.

The sodium salt of p-acetaminobenezene sulphonamide (27 g.) was taken in 25 c.c. of phenol and heated to 140°. Ethyl sulphocyanide (10 g.) was then gradually added and the mixture heated for 1 hour at 150-160°. Ammonium nitrate (9 g.) was then added and the mixture refluxed for 2 hours more. This was cooled and diluted with benzene when a solid separated out. This was filtered and washed with dilute alkali and then crystallised from water when p-acetaminobenzene sulphonylguanidine, m.p. 263° separated in clusters of needles. (Found : N, 22.0. $C_9H_{12}O_3N_4S$ requires N, 21.28 per cent).

30 G. of the above compound and 150 c.c. of 5% hydrochloric acid were heated on a wire guage for 35 minutes. It was cooled and made alkaline with dilute sodium hydroxide and the solid separating was crystallised from water, when p-aminobenzene sulphonylguanidine, m.p. 189° was obtained in clusters of needles.

Preparation of Sulphonamide-phenylsulphanilylguanidine.—The sodium salt of p-aminobenzene sulphonamide(9 parts) was taken in 18 parts of phenol and heated to 150°. Ethyl sulphocyanide (4 parts) was gradually added to the mixture and the heating continued for one hour more at 180°. The reaction mixture was cooled and diluted with benzene, filtered and the solid collected. The solid was dissolved in water and half neutralised with dilute hydrochloric acid when a solid separated out. This was purified by crystallisation from water (charcoal) in needle-shaped crystals, m.p. 216°. (Found : N, 18.84 $C_{13}H_{15}O_4N_5S_2$ requires N, 18.97 per cent).

This compound also separated out while preparing sulphanilyl cyanamide by reacting sodium salt of sulphanilamide with an alkyl sulphocyanide.

The paper is based on a pending patent application.

In conclusion the authors wish to express their sincere thanks to Dr. U. P. Basu for his interest in the course of these investigations.

CHEMICAL STUDY OF THE SEEDS OF SARDA

By S. Ali Ahmad and D. R. Dhingra

Component fatty acids of Sarda (Melon) seed oil excluding unsaponifiable matter (N-S) are myristic (2.0%), palmitic (2.0%), stearic (5.5%), arachidic (0.9), oleic (32.9%), linoleic (55.5%); N-S is 0.6%. The acids seem to be evenly distributed in the glycerides.

Sarda, a variety of *Cucumis melo*, Linn. (melon) grows abundantly in Afghanistan and Baluchistan. Its fruits and seeds are somewhat different in taste and bigger in size than those of the Punjab Kharbuz or melon (*cf.* Dhingra and Narain, *J. Indian Chem. Soc.*, 1945, 22, 123). Component fatty acids of Sarda seed fat and other constituents of their seeds have been examined and compared with those of Kharbuz seeds, with respect to varietal, climatic and soil differences.

Kernels contain 44.6% oil, 35.8% proteinous substances, 3.0% phosphates (P_2O_5), 5.6% ash. Thus they form a good substitution for the more expensive almond seed kernels, as an article of nourishing food. Oil also is of a pleasant odour and taste and light pale colour and can be used medicinally and as an article of food in place of the highly expensive almond oil.

EXPERIMENTAL

Sarda seeds were obtained from Quetta (Baluchistan) and oil from it was extracted with light petroleum ether. The data of the chemical examination of its seeds and fat are as follows :—

Seeds :   Moisture (9.0%), proteinous substances (25.2%), oil (24.9%).

Kernels :   Oil (44.6%), proteinous substances (35.8%), phosphates (P_2O_5, 3.0%), ash (5.6%) (ash contains iron, potassium, silica, phosphates and traces of calcium).

Oil :   Sp. gr. at 23.5°, 0.9174; Sap. equiv., 294.3; I.V. 125.5; A.V. 3.9; refractive index $n_D^{43.5}$ 0.4863; N-S., 0.6%.

Corresponding data of the Punjab Melon seed (*loc. cit.*) are :

Kernels :   Oil (40.0%), proteinous substances (22.8%), phosphates (P_2O_5), 0.3%.

Oil :   S.E., 270.0; I.V., 117.1; A.V., 0.9; N-S, 0.8%

Thus Sarda seed kernels form a source of richer food in every respect than those of Kharbuz kernels.

Component Fatty Acids

The oil (450 g.) was subjected to a detailed examination for their component fatty acids and the presence of these acids was confirmed according to the methods given in the study of Kharbuz oil (*loc. cit.*). Their final data along with those of the Kharbuz oil and Californian melon oil (Baughmann and Jamieson, *J. Amer. Chem. Soc.*, 1920, 42, 152) are given in the following table.

TABLE I

Cucumis melo seed oil

Acids.	Sarda (Baluchistan)	Kharbuz (Punjab)	Melon Californian (Cantaloup)
Caproic	—	1.0	—
Caprylic	—	2.0	—
Myristic	2.0	1.2	0.3
Palmitic	3.2	7.2	10.3
Stearic	5.4	0.2	4.6
Arachidic	0.9	—	—
Oleic	32.7	42.7	27.5
Linoleic	55.2	44.8	57.3
N-S	0.6	0.9	—
Association ratio (i.e., mols. unsaturated : mols. saturated acids)	7.21 : 1	5.62 : 1	—

From the above data, it is clear that the component acids of Baluchistan Sarda seed oil differ to some extent from the other two melon seed fats. Lower acids (caproic and caprylic) are found in the Punjab oil only but these are compensated by the higher percentage of higher saturated acids (stearic and arachidic) in the other two fats. Moreover, more highly unsaturated acid (linoleic) preponderates in Sarda oil like that in Californian oil. It seems that the soil and climate and varietal differences affect the metabolism of fats in seeds. Cold, dry climate and rocky dry soil of Quetta (Baluchistan) seem to help in the production of higher percentage of saturated acids of higher molecular weight and more highly unsaturated acids than the hot, somewhat humid climate and soft, alluvial soil of the Punjab. However, there is no fundamental difference in the two fats and there is a broad similarity in their having almost the same percentage of total unsaturated acids (about 88%) which preponderate and are characteristic of Cucurbitaceae family (Hilditch, *Allgem. Oel Fett. Ztg.*, 1930, 27, 184 219, 255).

Component Glycerides.—No fully saturated glycerides separated on cooling the acetone solution of the fat at 5° for five days.

SIR PRAFULLA CHANDRA RAY MEMORIAL FUND

The Honorary Secretary of the Indian Chemical Society acknowledges with grateful thanks the contributions received towards the Sir P. C. Ray Memorial fund.

The fund has been opened with the object of perpetuating the memory of Late Sir Prafulla Chandra Ray by creating an Endowment which will meet the expenses of the Annual Memorial Lecture. Below is given the names of the subscribers who have contributed an amount of Rs. 10- and above.

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Union Drug Co., Ltd., Cal. ...	200	0	0	Mr Sati Prasanna Sarkar, Cal.	50	0	0
Mr. J. M. Dutta, Cal. ...	100	0	0	Mr. R C. Prasad, Dharbhanga ...	50	0	0
,. Lilananda Gupta, Amritsar	125	0	0	Prof. P C Mitter, Cal ...	50	0	0
,, H. R Kapur, Amritsar ...	100	0	0	Prof. P Ray, Cal. ...	50	0	0
Seth Paul Virmani, Amritsar ...	100	0	0	Mr M N. Banerjee, Bihar			
Indian Health Institute, Cal. ...	100	0	0	Miscellany, Cal. ...	50	0	0
Adair Dutt & Co., Ltd., Cal. ..	100	0	0	Messrs Travancore Rubber Works	35	0	0
Messrs. Ogale Glass Works,				Mr H. B Chakravarti, Comilla			
Alwaye	100	0	0	Union Bank, Cal ...	30	0	0
Mr. B. L. Lalkaka, Pioneer				Mr S P Padmanabhan, Trivandrum	30	0	0
Magnesia Works, Bombay ...	100	0	0	Mr H. G. Ogden, Sheffield ...	28	0	0
Mr. B. P. Saxena, Cawanpore Chemical Works, Khasa ...	100	0	0	Prof S N. Bose, Dacca ...	25	0	0
Mr. R. S. Das Bhargava,				Dr. J. K Chowdhury, Dacca ...	25	0	0
Amritsar	100	0	0	Dr T R Seshadri, Madras ...	25	0	0
Mr. K. N. Bhandari, Indore ...	100	0	0	Hargolal & Sons, Amballa ...	25	0	0
Mr. P. C. Sanyal, Ballygunge				Dr S. S Deshapande, Indore ...	25	0	0
Chemical Works, Cal. ...	100	0	0	Dr. A. R. Normand, Bombay ...	25	0	0

	Rs	A.	P.
Dr. H. L. Roy, Jadavpur ...	25	0	0
Mr. J K. Bhattacharya, Shillong	25	0	0
Dr. M. L. Shah, Baroda ...	25	0	0
Dr. P. K. Bose, Namkum ...	25	0	0
Dr. R. C. Roy, Patna ..	25	0	0
Dr. K. G. Naik, Baroda ...	25	0	0
Mr. M. B. Amin, Baroda ...	25	0	0
Messrs Chandulal Keshavlal & Co., Baroda	25	0	0
Messrs. Baroda Chemical Industries Ltd., Baroda ...	25	0	0
Messrs. Dinabandhu Leather Industries, Baroda ...	25	0	0
Messrs. Ashwin Industries, Ltd , Baroda	25	0	0
Mr. P Viswanathan, Quilon .	25	0	0
Mr. T. K. Kuruvilla, Trivandrum	25	0	0
Mr. S. C. Karayalar, Trivandrum	25	0	0
Mr J. E A. Periera, Trivandrum	25	0	0
Prof N. K. Basu, Patna ...	25	0	0
Dr. P. B. Ganguly, Patna ...	20	0	0
Dr. B. N. Ghosh, Cal. ...	20	0	0
Dr D. K. Banerjee, Cal. ...	20	0	0
Mr R C. Ghosh, Cal ...	20	0	0
Mr R. P. Sanghi, Gorakhpur ...	15	0	0
Mr. D. N. Chatterjee, Benares ...	15	0	0
Industrial & Excise Lab., Baroda	15	0	0
Mr B. K. Bose, Cal ..	10	0	0
Mr V. Paul, Trivandrum ..	10	0	0
Mr K. R. Krishna Iyer, Trivandrum ...	10	0	0
Mr S. C. Gupta, Trivandrum ...	10	0	0
Mr. A. N Poti, Trivandrum ..	10	0	0
Mr. J. W. Cameron, Trivandrum	10	0	0
Mr. T. U. Phillipose, Trivandrum	10	0	0
The Vishnu Industrial Works, Baroda	10	0	0
Agricultural Chemists' Lab., Baroda ...	11	0	0
Dr. C. S. Patel, Baroda ...	10	0	0
Dr M. D. Avasare, Baroda ...	10	0	0
Mr. C. B. Patel, Baroda ...	10	0	0
Public Health Lab., Baroda	10	0	0

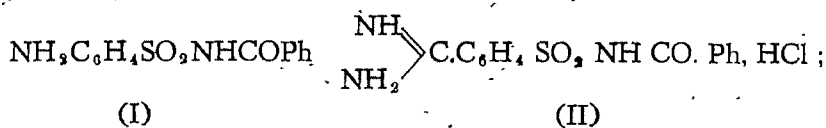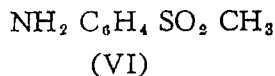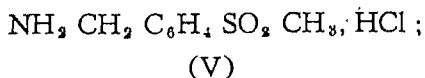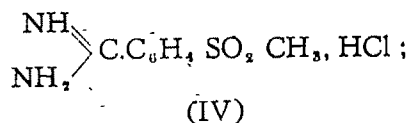|	Rs.	A	P.
The Star Chemical Works, Baroda	10	0	0
Mr. I. S. Amin, Baroda ...	10	0	0
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Dr. C. B Shah, Baroda ...	10	0	0
Mr V. C. Amin, Baroda ...	10	0	0
Messrs. D Naumbhai & Co., Baroda	10	0	0
Dr M P Shah, Baroda ...	10	0	0
Dr. C. C. Shah, Baroda ...	10	0	0
Prof D. V Chandroker, Jubbulpore	10	0	0
Prof. L. S Surrey, Jubbulpore	10	0	0
Mr F R Peermahamad, Bombay	10	0	0
Mr B. Chakravarti, Bahraich	10	0	0
Mr Lal Chand Chopra, Amritsar	10	0	0
Mr. A C. Sen, Amritsar ...	10	0	0
Mr. Ram Singh, Amritsar ...	10	0	0
Dr S S. Guha Sircar, Dacca	10	0	0
Mr. J H. Marsden, Cal. ...	10	0	0
Mr. Ganguly, Amritsar ...	10	0	0
Dr M. Goswami, Cal. ...	10	0	0
Dr. J. Gupta, Cal. ...	10	0	0
Dr. D Chakravarti, Cal. ...	10	0	0
Mr S. N. Mukherjee, Cal. ...	10	0	0
Dr. M. Q. Doja, Patna ...	10	0	0
Dr Asima Chatterjee, Cal. ...	10	0	0
Dr Bidyut Kamal Bhattacharya, Cal.	10	0	0
Dr. J C. Bardhan, Cal. ...	10	0	0
Dr. P. C. Datta, Cal. ...	10	0	0
Dr. S. G. Chaudhuri, Cal. ...	10	0	0
Major Charles Eric Wooten, Kirkee	10	0	0
Mr. N. L. Vidyarthi, Patna ...	10	0	0
Dr. P N. Das Gupta, Patna....	10	0	0
Mr P P Patel, Patna ...	10	0	0
Mr. S A Faseeh, Lucknow ...	10	0	0
Dr B L. Manjunath, Delhi ...	10	0	0
Dr A L. Sundara Rao, Delhi	10	0	0
Dr S. P. Raychaudhuri, New Delhi	10	0	0
Small Collections ...	745	0	0
Total ...	10,382	0	0

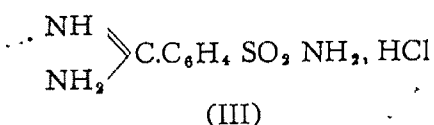# STUDIES ON SULPHONAMIDES AND ANALOGOUS COMPOUNDS

By J. Sikdar and U. P. Basu

Certain sulphonamides and sulphones have been prepared and described

It has been recently noticed by Swyer and Young (*Brit. Med. J.*, 1945, i. 149) and Bose and Ghosh (*Indian Med. Gaz.*, 1945, 80, 293) that N^1-benzoylsulphanilamide exerts a specific chemotherapeutic action against bacillary dysentery organisms. This compound is readily absorbed from the gastro-intestinal tract (*cf.* Bose and Ghosh, *Indian J. Med. Res.*, 1944, 32, 61); but it is the general belief that the efficacy of a sulphanilamide type of compound in bacillary dysentery is dependent on its low solubility and poor absorption from the upper alimentary tract (Marshall *et al.*, *Bull. Johns Hopk. Hosp.*, 1940, 67, 163; 68, 94). On this hypothesis certain acyl derivatives of sulphathiazol were also prepared and found to be effective (*cf.* Poth and Ross, *J. Lab. Clin. Med.*, 1944, 29, 785). It was considered to be of interest to study the influence of similar acyl substituents at the *para*-amino group of N^1-benzoylsulphanilamide. Accordingly N^4-acetyl-, -benzoyl, -succinyl, and -phthalyl derivatives were prepared and their bacteriostatic action against bacillary dysentery organisms (Flexner Y.) was noted.

As amidino group exerts a parasiticidal action, it was then introduced into the above sulphanilylbenzamide by replacement of its *p*-amino group. The resulting *p*-amidinobenzene sulphonbenzoylamide hydrochloride (II), the simple *p*-amidinobenzene sulphonamide hydrochloride (III) and the *p*-amidinophenylmethylsulphone hydrochloride (IV) were all studied. Recently the antibacterial activity of the compounds (III) and (IV) and *p*-(aminomethyl)-phenylmethylsulphone hydrochloride (V) has been recorded by Evans, Fuller and Walker (*Lancet*, 1944, ii, 523) against gas gangrene. These compounds were also prepared and their bacteriostatic action on dysentery organisms noted. In searching the literature it was noticed that the action of the simple sulphone, *p*-aminophenylmethylsulphone (VI) has not been studied against bacillary dysentery and as such this compound was also prepared (*cf.* Fourneau *et al.*, *Compt. rend. soc. Biol.*, 1938, 127, 393) and its *in vitro* activity was studied.

$$NH_2C_6H_4SO_2NHCOPh \qquad \underset{NH_2}{\overset{NH}{>}}C.C_6H_4\ SO_2\ NH\ CO.\ Ph,\ HCl\ ;$$

<center>(I)   (II)</center>

$$\begin{matrix} NH \\ NH_2 \end{matrix}\Big\rangle C.C_6H_4 \, SO_2 \, NH_2, \, HCl$$

(III)

$$\begin{matrix} NH \\ NH_2 \end{matrix}\Big\rangle C.C_6H_4 \, SO_2 \, CH_3, \, HCl \, ;$$

(IV)

$$NH_2 \, CH_2 \, C_6H_4 \, SO_2 \, CH_3, \, HCl \, ;$$

(V)

$$NH_2 \, C_6H_4 \, SO_2 \, CH_3$$

(VI)

The antibacterial action of the above compounds were studied on th e organism of bacillary dysentery (Flexner Y) by noting the inhibition of growth in a culture medium made from a papain-digest-glucose-phosphate broth when incubated for 72 hours at $37°$. In each case the inoculum used was about 1000 organisms in 5 c. c. of broth. The table below shows the minimal concentration expressed in mg. of drug per 100 c. c. of culture medium.

Minimal inhibiting concentration in mg. of drug per 100 c c. of culture medium

Organism	Compounds									
	(I)	(II)	(III)	(IV)	(V)	(VI)	Ac	Bz	Succ	Phthal
Flexner (Y)	10	100	100	100	20	100	100	100	100	200

Ac = Acetyl
Bz = Benzoyl   } derivative of sulphanilylbenzomide,
Succ. = Succinyl
Phthal = Phthalyl

It is evident from the table that none of the various compounds studied is superior to sulphanilylbenzamide.

EXPERIMENTAL.

Sulphanilybenzamide (N¹-*Benzoylsulphanilamide*) (I).—At first acetyl sulphanilylbenzamide was prepared by modified Schotten-Baumann method from *p*-acetylsulphanilamide and benzoyl chloride. The compound crystallised from dilute alcohol in needles, m. p. $251°$ (decomp.) (*cf.* Crossley *et al., J. Amer. Chem. Soc.,* 1939, 61, 2950). (Found : N, 9·11. Calc for $C_{15}H_{14}O_4N_2S$: N, 8.805 per cent).

The N⁴-acetylsulphanilylbenzamide was then hydrolysed by heating on a water-bath with caustic soda solution (6%) for 1hour. The cold solution was just neutralised with dilute hydrochloric acid when sulphanilylbenzamide precipitated out. It was filtered, washed with water and crystallised from rectified spirit in prisms, m. p. 181-82° (*cf.* Crossley *et al, loc. cit.*). (Found : N, 10.4. Calc for $C_{13}H_{12}O_3N_2S$: N, 10.15 per cent).

N^4-*Benzoylsulphanilylbenzamide* was prepared by benzoylating sulphanilylbenzamide by the Schotten-Baumann method as above. On acidifying the alkaline solution of the bezoylated product, the dibenzoyl derivative precipitated out. It was filtered, washed with water and then boiled with water, filtered hot and washed with hot water. The product was then crystallised from alcohol. It melted at 258° (decomp.) (*cf*. Chien-Pen-Lo, *et al*., *J. Amer. Chem. Soc*., 1944, 66, 660) (Found : N, 7.54. Calc for $C_{20}H_{16}O_4N_2S$: N 7.37 per cent),

N^4-*Succinylsulphanilylbenzamide*.—Finely powdered succinic anhydride (1 mol.) was gradually added to a boiling suspension of sulphanilylbenzamide (1 mol.) in absolute alcohol. After the addition was over, the solution was refluxed for 1 hour on a water-bath. A crystalline solid separated out. The product was cooled, filtered, washed with a little alcohol and crystallised from alcohol, m. p. 214°. (Found : N, 7.61, $C_{17}H_{16}O_4N_2S$ requires N, 7.45 per cent).

N^4-*Phthalylsulphanilylbenzamide*.—Sulphanilylbenzamide (5g.) was dissolved in 50 c. c. of absolute alcohol by boiling and freshly sublimed and finely powdered phthalic anhydride (2.7 g.) was added in small quantities at a time to the boiling solution. The solution was then refluxed for 2 hours and cooled. A white crystalline compound separated. It was filtered, washed with alcohol and crystallised from acetone, m, p. 224-25°. (decomp.). (Found : N, 6.56. $C_{21}H_{16}O_6N_2S$ requires N, 6.6 per cent).

p-Amidinosulphanilylbenzamide Hydrochloride (II).—Powdered *p*-cyanosulphanilylbenzamide (7 g.) (prepared by benzoylating *p*-cyanosulphanilamide in our modified Schotten-Baumann method) was dissolved in 300 c. c. of absolute alcohol and dry hydrochloric acid gas was passed through the solution, cooled in ice, till saturated. The solution was then kept in the refrigerator for 4 days. A white crystalline compound separated which was filtered, washed with absolute alcohol, powdered and added to 50 c. c. of alcohol, saturated with ammonia gas and the solution was kept at the room temperature for 6 days. A crystalline compound separated. It was filtered, washed with alcohol and crystallised from concentrated hydrochloric acid, m. p. 210-11°. (Found : N. 12.62 ; Cl, 10.24. $C_{14}H_{13}O_3N_3S$, HCl requires N. 12.37; Cl, 10.45 per cent).

p-Amidinobenzenesulphanilamide Hydrochloride (III).—*p*-Cyano-sulphanilamide was dissolved in absolute alcohol and proceeding exactly in the same manner as in the previous example, the *p*-amidinobenzene-sulphonamide was isolated. The substance was crystallised from concentrated hydrochloric acid, m. p. 242-44°. (Found : N. 17.98 ; Cl, 14.82. $C_7H_9O_2N_3S$, HCl requires N, 17.83 ; Cl, 15.07 per cent).

p-*Amidinophenylmethylsulphone Hydrochloride* (IV).

(*i*) *Acetylaminophenylmethylsulphone.*—Finely powdered sodium salt of p-acetylaminobenzenesulphinic acid (I) (Organic Syntheses, Vol. V, p 1) was suspended in alcohol. Methyl iodide dissolved in alcohol was added drop by drop to the boiling suspension of the sodium sulphinate. After the addition was over the solution was refluxed for 1 hour. It waa then filtered, the alcohol evaporated off from the filtrate and the solid residue thus obtained was treated with water, filtered, washed with water and crystallised from water, as white needles, m. p. 186-87°. (Found : N. 6.69. $C_9H_{11}O_3N$ requires N, 6.57 per cent).

(*ii*) p-*Aminophenylmethylsulphone.*—p-Acetylaminophenylmethylsulphone was refluxed with 25 times its weight of 10% hydrochloric acid for 1 hour. The solution was cooled, filtered and neutralised with dilute ammonia. The precipitate was filtered, washed with water and crystallised from water in small plates, m. p. 137°. (Found : N, 8.26. $C_7H_9O_2NS$ requires N, 8.18 per cent).

(*iii*) p-*Cyanophenylmethylsulphone.*—p-Aminophenylmethylsulphone was diazotised in the usual way and the diazotised solution was treated with copper cyanide in potassium cyanide solution with stirring. Then the mixture was heated to 70° for ½ hour, cooled and filtered. The product thus obtained was crystallised from a large volume of water as colourless needles, m. p. 144-45°. (Found : N, 7.85. $C_8H_7O_2N$ S requires N, 7. 73 per cent).

(*iv*) p-*Amidinophenylmethylsulphone hydrochloride* was prepared in the usual method as described in the preparation of p-amidinosulphanylbenzamide and crystallised from concentrated hydrochloric acid. It melted at 288°. (Found : N, 12.06 ; Cl, 14.83. $C_8H_{10}O_2N_2S$, HCl requires N, 11.94 ; Cl, 15.1 per cent).

p-*Aminomethylphenylmethylsulphone Hydrochloride* (V).—Benzyl acetamide was treated with chlorosulphonic acid in the usual way. The sulpho-chloride thus obtained was reduced with sodium sulphite (*cf-* "Organic Syntheses", Vol. V, p. 1) and the sulphinic acid was converted into the sodium salt. The sodium salt of p-(acetylamino-methyl) benzene sulphinic acid was boiled with alcohol and an alcoholic solution of methyl iodide was added drop by drop. After the addition was over the solution was refluxed for 1 hour, filtered, and the alcohol evaporated off. The solid residue thus obtained was treated with water, filtered, washed with water and dried. It had a melting point of 122°. The crude product was directly hydrolysed by refluxing for 1 hour with 25 times its weight of dilute hydrochloric acid. The solution was filtered and concentrated

by evaporation and cooled when a crystalline compound separated. It was filtered, washed with a little water and crystallised from water in flakes, m. p. 265°. (Found: N, 6.44; Cl, 15.7. $C_8H_{11}O_2NS$, HCl requires N, 6.32; Cl, 16.02 per cent).

The authors wish to thank Mr. P. Sen-Gupta for conducting the bacteriostatic action of the compounds.

DIMORPHISM IN SULPHANILYLBENZAMIDE DERIVATVES

By U. P. Basu and J. Sikdar

Alkyl derivatives of sulphanilylbenzamide exist in dimorphic forms. Method of isolation and general properties have been recorded.

N[1]-Benzoylsulphanilamide (sulphanilylbenzamide) has recently been shown (Swyer and Young, *Brit. Med. J.*, 1945, i, 149 ; Bose and Ghosh, *Indian Med. Guz.*, 1945, 80, 293) to be efficacious against bacillary dysentery. The entrance of this drug into the field of chemotherapy led us to make a survey of its physical and chemical properties. In the course of this study the compound was converted nto its silver salt and was subsequently treated with alkyl halides. The latter reaction afforded alkylated sulphanilylbenzamide but it was found that this compound occurred in two distinct crystalline forms. The conditions for the isolation of these dimorphs and their general properties are herein recorded.

EXPERIMENTAL
Reaction with Ethyl Iodide.

Sulphanilylbenzamide was crystallised from alcohol (95%) and obtained in fine prismatic needles, m. p. 181-82° (uncorrected) (Fig. 1). This was dissolved in calculated amount of 2N- caustic soda solution, cooled and slowly treated with freshly prepared silver nitrate solution. The silver salt at once precipitated out, was filtered, washed with water to make it free from silver ion and then with absolute alcohol and dried in *vacuo* in the dark. It gradually acquired a tint on exposure to light

The silver salt was then suspended in dry benzene and refluxed with ethyl iodide (1. 25 mole) for 1 hour. Silver iodide was found to separate out. The reaction mixture was filtered, and the filtrate was evaporated under diminished pressure to remove most of the benzene when crystals began to separate. On cooling, crystals were collected and dried over a blotting paper, and recrystallised from dilute alcohol (1:1) in fine elongated rectangular rods (Fig 2). It melted at 183° (uncorrected).

The filter from the above reaction mixture was extracted with alcohol (95%) by refluxing. The alcoholic solution was filtered and concentrated on a boiling water-bath. Crystals separated out. These were collected and recrystallised from dilute alcohol (1:1) in hexagons, m. p. 189° (uncorrected) (Fig. 3). An analysis of both types of crystals for nitrogen and sulphur gave the following results.

[Found (rectangular rods, m. p. 183°) : N, 9·53 ; S, 10·45. (hexagons, m. p. 189°) : N, 9·49 ; S, 10·41, $C_{15}H_{16}O_3N_2S$ requires N, 9·2 ; S, 10.52 per cent).

The yield-ratio of 'Rods' variety to "Hexagons" was about 20 : 50.

General Properties.—Both forms are insoluble in water, readily dissolve in alkali and are precipitated on acidification. They are partly soluble in acids but neither the soluble portions nor the insoluble parts give diazo reaction. Both respond to secondary amine test. A mixture of the two in equal proportion melts indifferently at 165°.

They were then subjected to acid-hydrolysis. For this 0.5 g. of each form was refluxed with 20 c.c. of 10% hydrochloric acid for 5 hours. The container was cooled when a white crystalline substance separated out. This was identified as benzoic acid. The filtrate was neutralised with sodium carbonate when another white substance was precipitated. This was collected and crystallised from boiling water (charcoal). The crop isolated from "Rectangular rods" separated in rhombic plates, m. p. 135° (Fig. 4) and the one obtained from "Hexagons" was leaf-like in structure, melting at 137° (Fig. 5). A mixture of the two in equal proportion melted at 111-14°.

An analysis of both types of these crystals for nitrogen again gave the following results :—

[Found (Rhombic plates, m. p. 135°) : N. 13.98. (Leaf-like crystals, m. p. 137°), N, 14.09. C_2H_5 NH. $C_6H_4SO_2$ NH_2 requires N, 14.0 per cent]

Both are partly soluble in water, readily dissolve in alkali, and partly soluble in dilute acid. The acid solution, however, gave no diazo reaction. In consulting the literature it was noticed that N^1-ethylsulphanilamide is of prismatic needles and melts at 106-107° (Mangini, *Chem. Abs.*, 1943, **37**, 98). One N^4-ethylsulphanilamide has been isolated by us by reacting silver salt of sulphanilamide with ethyl iodide (described in another paper), and found to melt at 135° without sintering when admixed with the rhombic plates as previously isolated by hydrolysis of the rectangular rods variety of ethyl sulphanilylbenzamide.

Reaction with Methyl Iodide.—Similarly silver salt of sulphanilylbenzamide was reacted with methyl iodide in benzene suspension as in the previous case. The benzene filtrate afforded a small quantity of a crystal, m. p. 155°, whereas the filter on extraction with alcohol (95%) gave a good yield of another product crystallising from dilute alcohol (1 : 1) in fine needles, m. p. 142°.

They on analysis gave nitrogen, 9·81 and 9·74% respectively. Methyl derivative of sulphanilylbenzamide ($C_{14}H_{14}O_3N_2S$) requires N, 9·65 %.

Neither is soluble in acids but each readily dissolves in alkali. On hydrolysing the crop, m. p. 142°, by dilute hydrochloric acid as usual, benzoic acid separated out on cooling. The hydrolysed solution on neutralisation with

sodium carbonate afforded N^4- methyl sulphanilamide. This crystallised from dilute alcohol in rectangular plates, melting at 210-11^b (uncorrected). To ascertain its constitution silver salt of sulphanilamide was refluxed with methyl iodide in benzene suspension for 2 hours. The reaction mixture was filtered and the benzene solution was allowed to cool. Crystals separating were collected and recrystallised from dilute alcohol. It melted at 210-11° without depressing when mixed with equal part of the above N^4-methylsulphanilamide, the corresponding N^1-methylsulphanilamide melting at 111-12° (cf. Mangini, loc. cit.).

It may be noticed that when the silver salts of the N^1-benzoyl-sulphanilamide (sulphanilylbenzamide) are reacted with an alkyl iodide, the N^4-hydrogen atom is always being substituted by the alkyl radical. The alkylated compounds obtained are soluble in alkali and form silver salts, but the latter, no more react with ethyl iodide and may be recovered practically unchanged from the reaction mixture. Similarly N^4-acetyl-N^1-benzoylsulphanilamide is soluble in alkali, forms silver salt but cannot be further alkylated.
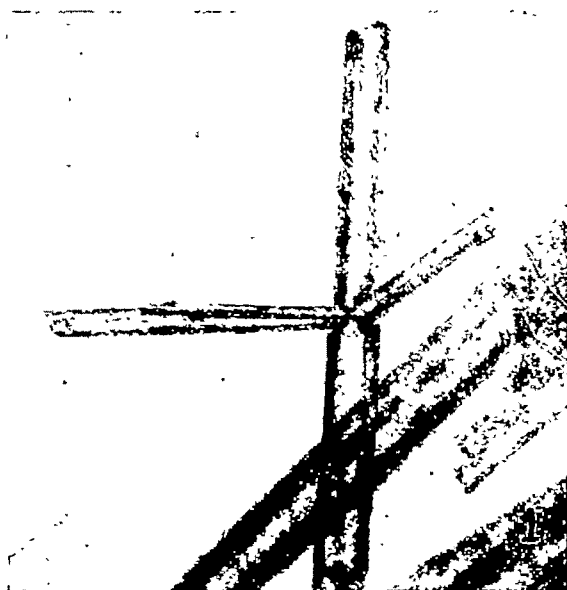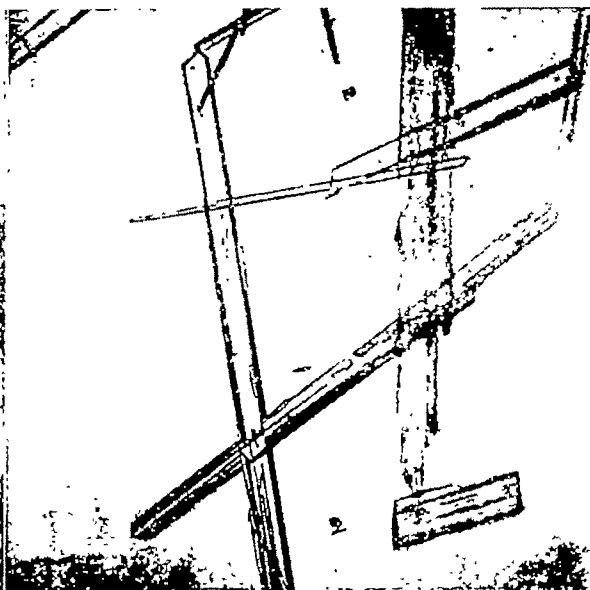
Fig. 1
Sulphanilylbenzamide (× 80)

Fig 2.
N⁴-Ethyl sulphanilylbenzamide (× 80)

Fig. 3.
N⁴-Ethyl sulphanilyl-
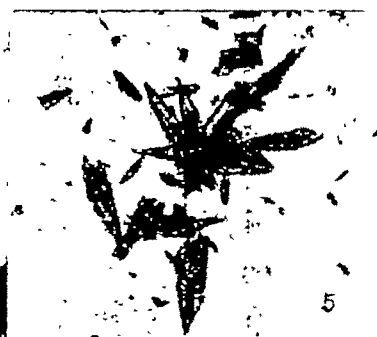benzamide (× 225)

Fig. 4.
N⁴-Ethyl sulphanilamide
(× 225)
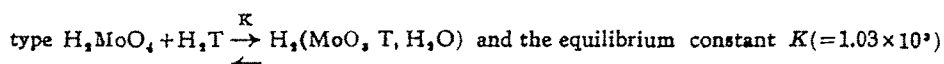
Fig. 5.
N⁴-Ethyl sulphanilamide
(× 100)

PHYSICO-CHEMICAL STUDIES OF COMPLEX FORMATION BETWEEN MOLYBDIC ACID AND TARTARIC ACID. PART I. POLARIMETRIC STUDIES

BY ANIL BHUSAN BISWAS

The complex formation between tartaric and molybdic acids in solution has been studied polarimetrically. The reaction is shown to be governed by an equilibrium of the type $H_2MoO_4 + H_2T \xrightleftharpoons{K} H_2(MoO_3 T, H_2O)$ and the equilibrium constant $K(=1.03 \times 10^3)$ has been calculated. The reaction goes to completion when the concentration of one of the components is 4 times the other. The possible causes for exalted rotation and other peculiarities have been discussed and a probable constitution of the complex compound is given in keeping with the co-ordination theory of valency.

The peculiarities of optical rotatory powers and rotatory dispersions of tartaric acid and its derivatives have attracted considerable attention ever since they were first discovered by Biot. Garnez (*Compt. rend.*, 1887, **104**, 785 ; 105, 85 ; 1889, 108, 942) investigated the changes in rotatory power of solutions of tartaric acid in presence of alkali molybdates of varying concentrations and obtained maximum rotations when the acid and the salt were in equimolecular proportions and suggested the formation of definite complex. Rosenheim and Itzig (*Ber.*, 1900, 33, 707) considered the complex as containing one molecule of sodium tartrate and varying amounts of molybdic oxide, viz. 1,2,2.4,4, etc. Itzig (*ibid.*, 1901, 34, 1372) added varying amounts of either sodium molybdate or ammonium paramolybdate to the solution of hydrogen tartrate and came to the same conclusion. Klason and Kohler (*Ber.*, 1901, 34, 3946) extended Itzig's work and found that the maximum rotation given by sodium hydrogen tartrate depends on other factors besides the amount of alkali metal such as the proportion of molybdic acid, the concentration of the active substance and the temperature of the solution. The work was subsequently taken up by many, notably Mazzucchalli (*Atti. R. Accad. Lincei*, 1910, 19, ii, 439 ; *Gazzetta*, 1913, 43, ii, 26), Grossman (*Ber.*, 1903, 36 1606 ; 1905, 38, 3874 ; *Z. anorg. Chem.*, 1904, 41, 43 ; 1908, 60, 50), Rimbach (*Z. anorg. Chem.*, 1907, 53, 397 ; 1922, 100, 393), Darmois (*Compt. rend.*, 1923, 176, 1140 ; 1924, 179, 629 ; *Bull. Soc. chim.*, 1928, 43, 1214), Britton and Jackson (*J. Chem. Soc.*, 1934, 1055), Yeu ki Heng (*J. chim. phys.*, 1936, 33, 383) and Delsal (*J. chim. phys.*, 1938, 35, 350).

The conclusions reached by these authors are conflicting and sometimes questionable excepting the indications of the formation of a definite complex. As regards the molecular proportion of the two components in the complex, some workers have assumed the ratio to be one and some, more than one,

dependent on the proportion in which they are present in the mixture. The difficulty to decide the problem is the continuous failure to get the compound in a well-crystallised solid state of fixed composition. Although in a very few cases crystallisation was tried, the composition of the product was found to vary. Compounds of the general formula $R_2(XO_3)C_4H_4O_6$ [R = alkali metal, X = Mo] have been prepared by Rosenheim and Itzig (loc. cit.) in crystalline form ; on the other hand Handerson and Barr (J. Chem. Soc., 1896 69, 1455) prepared a series of salts of the composition XO_2 (Na $C_4H_4O_6$)$_2$.

Most of the previous studies suffer from the defect that two or more variables, which have a pronounced influence on optical rotation, have been superimposed upon one another. The presence of alkali metals or NH_4^+ ions. either as a salt of any of the two component acids or as a free base, may change the rotation value considerably ; the pH of the system also is a very important factor in this connection. Moreover, studies on the optical rotation were confined to one wave-length only, but it is known that complex compounds behave anomalously toward light ; in one wave-length it may seem inactive, while for shorter or longer wave-lengths it may show activity in different directions. Therefore, it is risky to draw any conclusion from studies of rotations at one particular wave-length.

The object of the present investigation is to study in detail, the peculiarites of optical rotations manifested on the addtion of d-tartaric acid to a molybdic acid sol avoiding the above mentioned shortcomings, to determine the reaction and the composition of the reaction product that is formed. The optical rotations were measured at four different wave-lengths.

E X P E R I M E N T A L

The optical rotations were measured in a triple field polarimeter which gave the values with an accuracy of $\pm 0. 01^0$. The wave-lengths selected were 690 $\mu\mu$, 578 $\mu\mu$, 546 $\mu\mu$ and 436 $\mu\mu$. The wave-length 690 $\mu\mu$ was taken out from an ordinary electric lamp with the help of a suitable filter and for the other three, mercury arc lamp was used form which the respective wave-lengths were isolated with suitable filters. Molybdic acid (MoO_3) was used in colloid form, carefully purified by dialysis, d-tartaric acid (H_2T) (B.D.H. product) was further purified by recrystallisation. Redistilled water was always used for making solutions.

In Table I are shown the values for optical rotation obtained by adding increasing amounts of MoO_3 to a definite quantity of tartaric acid and the reverse of that, is followed and noted in Table II. The length of the polarimeter tube was always 0. 54 dm. and the temperature was 25^0.

The change in the nature of rotatory dispersion of pure tartaric acid solution, brought about by the addition of molybdic acid, is represented graphically in Fig. 1.

FIG. 1

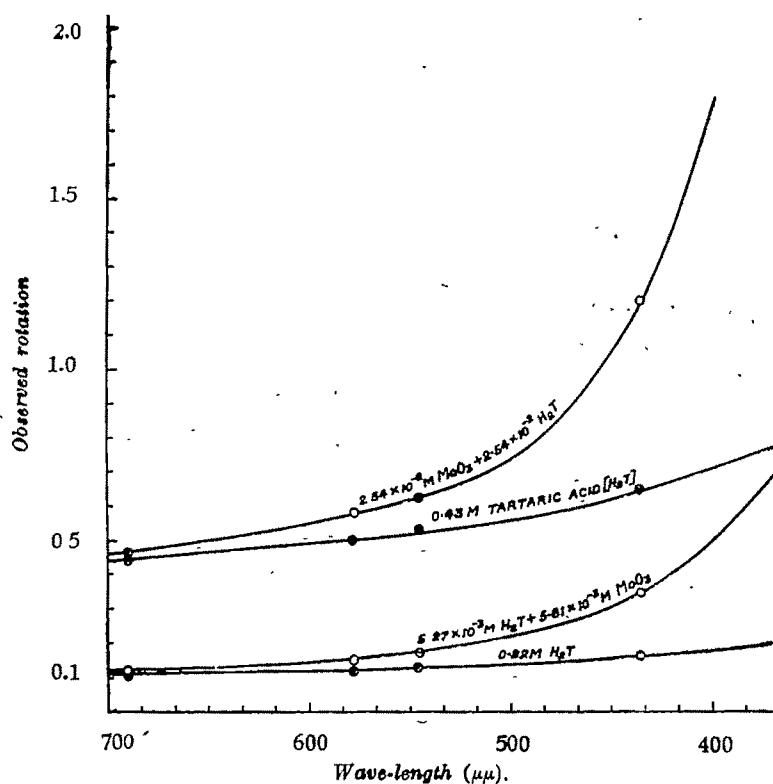*Rotatory dispersion of tartaric acid & complex molybdo-tartaric acid.*

TABLE I

Conc. of $H_2T = 5.27 \times 10^{-3} M$

	Ratio $\dfrac{MoO_3}{H_2T}$	$690\mu\mu.$	$578\mu\mu.$	$546\mu\mu.$	$436\mu\mu.$
1	0.25	+0.04	+0.05	+0.05	+0.08
2	0.50	+0.05	+0.06	+0.07	+0.14
3	0.75	+0.07	+0.09	+0.11	+0 21
4	1.00	+0.08	+0.10	+0 12	+0.22
5	2.00	+0.11	+0.14	+0.15	+0.29
6	3.00	+0.11	+0.14	+0 17	+0.32
7	4 00	+0.12	+0.15	+0.17	+0.33
8	5 00	+0.12	+0.15	+0 17	+0.33
9	6.00	+0.12	+0.15	+0.17	+0.33

TABLE II

Conc. of $MoO_3 = 2.53 \times 10^{-2} M$

Ratio H_2T/MoO_3		Rotation at wave-lengths (obs.)			
		690$\mu\mu$.	578$\mu\mu$.	546$\mu\mu$.	436$\mu\mu$.
a.	0.25	+0.12	+0.19	+0.21	+0.41
b	0.50	+0.25	+0.35	+0.38	+0.80
c.	0.75	+0.35	+0.48	+0.52	+1.01
d.	1.00	+0.46	+0.58	+0.62	+1.18
e	2 00	+0 63	+0.77	+0.85	+1.59
f.	3 00	+0.69	+0.89	+0.99	+1.83
g	4.00	+0.80	+0.98	+1.10	+2.02
h.	5,00	+0.84	+1.02	+1.15	+2.08
i	6 00	+0.86	+1.07	+1.19	+2 12

It will be noticed in Table I that increased addition of MoO_3 increases the rotation gradually in all the wave-lengths terminating with a constant maximum, when the concentration of MoO_3 is about 4 times that of H_2T, and it seems that MoO_3 does not go into reaction any more after that. Referring to Table II, it is found that the rotation increases as before and after the value 4 is reached for the ratio H_2T/MoO_3, the values increase slowly, probably due to H_2T remaining completely unreacted. In the later part of Table II if the rotation values given by H_2T, when present separately at the same concentration as in the respective mixtures, be subtracted from the observed values of the mixtures, the resulting figures should remain constant from the stages where the extra amount of H_2T added would remain completely uncombined. The results of such subtractions are given in Table III, and it will be seen that the rotation becomes steady after the value for the ratio H_2T/MoO_3 is 4.

## TABLE III

Optical rotation at different wave-lengths.

	690$\mu\mu$.			578$\mu\mu$.			546$\mu\mu$.			436$\mu\mu$.		
	Obs.	Due to H_2T	Diff.	Obs.	Due to H_2T	Diff.	Obs.	Due to H_2T	Diff.	Obs.	Due to H_2T	Diff.
(f)	+.69	+.07	+.62	+.89	+ 08	+.81	+ 99	+.11	+ 88	+1 83	+.13	+1.70
(g)	+.80	+.10	+.70	+ 98	+.11	+.87	+1·10	+.13	+.97	+2.02	+.16	+1.86
(h)	+.84	+.12	+.72	+1.02	+.15	+.87	+1.15	+.16	+.99	+2.08	+.20	+1.88
(i)	+.86	+.15	+.71	+1.07	+.19	+ 88	+1 19	+.20	+ 99	+2.12	+.25	+1.87

The increase of rotation with the increase in the concentration of MoO_3 has been assumed by several workers to be due to the formation of new

compounds of composition varying from $Na_2(MoO_3)C_4H_4O_6$ to $Na_2(MoO_3)_4$ $C_4H_4O_6$; Britton and Jackson (*loc. cit.*) suggested the probable equilibrium reaction of the type

$$Na_2(XO_3)C_4H_4O_6 + XO_3 \rightleftharpoons Na_2(XO_3)_{x+1}C_4H_4O_6 ; \quad (X = Mo)$$
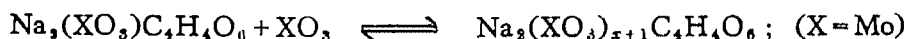
There is no justification for assuming a new compound each time the rotation value changes. On the other hand from our observations in Tables I and II, we are led to believe that the reaction between the two acids is governed by an equilibrium of the type

$$H_2T + H_2MoO_4 \rightleftharpoons H_2[MoO_3T, H_2O].$$
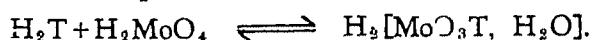
The observed facts can be easily explained on the formation of this complex acid which has much higher molecular rotatory power than pure H_2T. The increase of the concentration of either of the components will help the formation of the complex more and more showing increased rotation and the reaction becomes complete when the concentration of either of the components is about 4 times the other, indicated by the steady rotation value observed after that stage.

Assuming equimolecular combination and the applicability of the law of mass action,

$$K = \frac{[H_2(MoO_3T, H_2O)]}{[H_2T][H_2MoO_4]} = \frac{[Complex]}{[H_2T]_{free}[MoO_3]_{free}} \quad \ldots \text{(i)}$$

Observed rotation of any mixture = (molecular rotation of the complex) ×

[complex] + (molecular rotation of free H_2T) × $(H_2T)_{free}$ ... (ii)

For mixtures giving maximum rotations, [complex] = [H₂T],
when MoO_3 is in excess.

Then observed max. rotation = (mol. rotation of complex) × [H₂T]

$$\therefore \text{Molecular rotation of the complex} = \frac{\text{Obs. max. rotation}}{[H_2T]} \quad \ldots \text{(iii)}$$

$$\text{Similarly, mol. rotation of free } H_2T = \frac{\text{Obs. rotation of free } H_2T}{[H_2T]} \quad \ldots \text{(iv)}$$

and in any intermediate mixture, the concentration of free H_2T is given by

$$[H_2T]_{free} = \text{Total conc. of } H_2T - [complex] \quad \ldots \text{(v)}$$

Applying the above 5 equations to the data in Table I, the equilibrium constant K has been calculated as shown in Table IV below.

TABLE IV

	Wave-lengths			
Molecular rotaions (for 0.54 dm. tube)	690$\mu\mu$.	578$\mu\mu$.	546$\mu\mu$.	436$\mu\mu$.
Complex acid	22.8	28.4	32.2	62.6
H₂T (free) (calc. from actual rotation measurements)	1.01	1.15	1.24	1.52

TABLE IV—(contd.)

Solution Number in Table I.   Equilibrium constant $K \times 10^{+3}$

2	1.08	0.86	0.90	1.26
4	0.82	0.86	1.15	1.00
5	1.13	1.46	0.89	0.98

Mean $K = 1.03 \times 10^3$

It is found that the values of K obtained, are fairly constant supporting the validity of our assumptions. Now, from the known values of K and concentrations of both H_2T· and MoO_3, the concentration of the complex acid and free H_3T in any mixture can be calculated and hence the rotation value to be observed in such solutions can be precalculated from equation (ii) mentioned above. In Table V we have compared the rotation value thus calculated with that actually observed to test further the truth of our assumptions made before.

TABLE V

Conc. of $H_3T \times 10^5$.	Conc. of $MoO_3 \times 10^5$.	Rotations ($\mu\mu$) at							
		690$\mu\mu$.		578$\mu\mu$.		546$\mu\mu$.		436$\mu\mu$.	
		Calc	Obs.	Calc	Obs.	Calc.	Obs.	Calc.	Obs.
7.635M	3.832	+.075	+.08	+.095	+ 10	+.11	+ 11	+.20	+ 21
„	10.89	+.145	+.15	+.18	+.18	+.205	+.21	+.40	+.42
7.29	4.39	+.09	+.08	+.11	+.10	+.12	+ 12	+.235	+.22
„	17.60.	+.16	+.16	.+.20	+.19	+.225	+ 22	+.44	+ 43
5.907	23.63	+.13	+.12	+.16	+.15	+.18	+ 17	+.35	+.33
23.63	„	+.45	+.43	+.56	+.54	+.63	+.62	+1.23	+1.26
9.437	18.06	+.19	+.18	+.24	+.22	+.27	+.25	+.53	+.50
20.31	„	+.40	+.38	+.49	+.47	+.55	+ 53	+1.06	+1.07
76.12	25.37	+.62	+.60	+.77	+.74	+.87	+.83	+1.64	+1.60

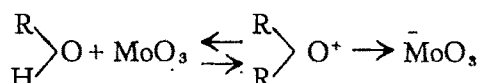It will be noticed that the calculated and observed values are of the same order.

DISCUSSION

The reaction between molybdic and tartaric acids is a moleculer one, one molecule of each combining together. We were at first led to think like that seeing the analogous rotatory power effected by the compound from the antimonius acid and tartaric acids, in which the complex compound is isolable and the emetic (potassium antimonyl tartrate) includes the two acids in the proportion $1:1$. Our assumption is also amply justified by the observations made above (Tables IV and V).

The change in the nature of the rotatory dispersion curve and large exaltation of optical rotations of H_3T, brought about by the addition of MoO_3, is due to a complex compound formation governed by an equilibrium reaction. But the nature of the combination is not revealed from such empirical representations, and we have discussed below this aspect of the reaction.

The cause of enhanced rotation may be explained in two ways, viz., (1) the reaction between the two acids takes place in such a way that a new centre of dissymmetry is formed or (2) the H_2T consists of two labile forms of oppositely rotatory dynamic isomers, one form of which preferentially reacts with the complete suppression of the other.

Now according to hypothesis (1) the union between the two acids may take place, thus :

$$\begin{array}{c}R \\ \\ H\end{array}\!\!\!>\!\!O + MoO_3 \underset{\longrightarrow}{\overset{\longleftarrow}{}} \begin{array}{c}R \\ \\ R\end{array}\!\!\!>\!\!O^+ \longrightarrow \bar{M}oO_3$$

Molybdenum shows variable valency and it can easily take up electrons ; here the combination has taken place with a semi-polar bond and a new centre of dissymmetry is formed round the positively charged oxygen atom. The latent optical activity, associated with the oxygen atom, is thereby developed to show enhanced activity. Support is given to this hypothesis by the structurally similar compounds of Phillips and co-workers (*J. Chem. Soc.*, 1925, **127**, 2352 ; 1926, 2079 ; 1927, 188 ; 1928, 3000) who have assigned the structure $\begin{array}{c}R' \\ \\ R'\end{array}\!\!\!>\!\!S^+ \rightarrow O^-$ to the sulphoxides which have comparable rotatory power. Burgess and Hunter (*ibid.*, 1929, 2838) accounted for the behaviour of borotartaric acid on a similar hypothesis, But in a number of cases this is untenable, It fails to explain why many other hydroxyl compounds are without any influence and also stand against the general tendency of the organic hydroxy-acids to form closed chain compounds.

Much more probable is the other hypothesis (2) where the existing equilibrium condition of the two dynamic isomers of tartaric acid is assumed to be disturbed by the presence of MoO_3, the latter being capable of combining with one of the isomers only, In that case the second isomer is gradually transformed into the reactive form to maintain the equilibrium condition. Thus, in certain circumstances the whole of H_2T in the solution may combine with MoO_3 to give rise to simple rotatory dispersion. The anomalous rotation of H_2T itself has been explained on the hypothesis (Lowry and Austin, *Phil. Trans.*, 1922, A, **222**, 249 ; Bancroft and Davis, *J. Phys. Chem.*, 1930, **34**, 897) that the observed rotatory power of H_2T is due to the difference of two much larger and nearly equal rotation values of two labile isomers in H_2T, and these are responsible for the small variation of optical rotation against wave-length, Lucas and Schowb (*J. Chem. Phys.*, 1932, **3**, 52) came to the same conclusion from spectrographic studies of H_2T.

On the Bohr theory of atomic structure, molybdenum $(1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^5 5S)$ like Cr, Fe, Ni and Pt, etc., which form well-defined compound of co-ordination number 6, is a member of one of the group of elements, the planetary electrons of which are undergoing reorganisation to show variable valency and marked colour in its compounds. Co-ordination number 8 also is exhibited in compound of the type $R_4[Mo(CN)_8]^{IV}$, and marked stability associated with the complex ion $[Mo(CN)_8]^{IV}$, is due to the fact that the cyanide units are regularly distributed round the central atom with effective atomic number 54, the same as that of Xenon. But the molybdotartrate compound is not so stable and is susceptible to easy reduction and so in all probability the complex compound is formed of an incomplete shell with co-ordination number 6, as shown below.

The X-ray analysis of $Ag_2[MoO_4]$ by Wyckoff (*J, Amer. Chem. Soc.,* 1922, 44, 1994] has disclosed oxygen atoms are tetrahedrally distributed round the central Mo atom and accordingly we can represent molybdic

acid as H
$$\left[\begin{array}{c} O \\ \uparrow \\ O—Mo—O \\ \downarrow \\ O \end{array} \right]$$
H and co-ordination with H,T occurs forming

a compound as,
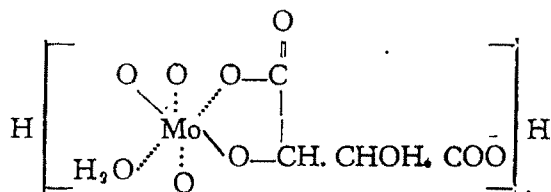
a five membered ring compound is formed with a molecule of H_2O within the co-ordination sphere. The corresponding oxalate compound crystallised as pyridine salt by Spittle and Wardlaw (*J. Chem. Soc.,* 1927, 1807) and Rosenheim (*Z. anorg, Chem,* 1896. 11. 225) was found by analysis to have a composition $RH[MoO_3, C_2O_4, H_2O]$.

My grateful thanks are due to Sir J. C. Ghosh for his kind interest and helpful criticisms in this work.

ACTION OF SULPHUR MONOCHLORIDE AND SULPHUR DICHLORIDE ON NAPHTHALENE DERIVATIVES AND ON ANTHRACENE

By J. W. Airan and S. V. Shah

As a result of the interaction between sulphur mono- and dichlorides on the one hand and naphthalene derivatives and anthracene on the other, naphthalene dithiochloride, anthracene tetrathiochloride, 4 : 4'-dihydroxydinaphthyl sulphide are prepared. In the same manner thio compounds of α- and β-naphthylamines are obtained, which have been assigned provisional structures.

Although the action of chlorides and oxychlorides of sulphur on aliphatic and benzene derivatives has been studied by various workers (Lorand, *Ind. Eng. Chem*, 1927, 19, 733 ; Gurthie, *Quart. J. Chem. Soc*, 1860, 12, 116 ; Smythe and Forster *J. Chem. Soc.*, 1910, 97, 1195 ; Cohen and Skirrow, *ibid.*, 1879 75, 887 ; Naik, *ibid.*, 1921, 119, 1166 ; Schmidt, *Ber.* 1878, 11, 1169 ; Coffey, *Rec. trav. chim.*, 1921, 40, 747 ; Ray, *ibid.*, 1921, 119, 1956), little work appears to have been done on anthracene, and naphthalene derivatives. Therefore a systematic study of these compounds containing $-OH$, $-CO_2H$, $-COCH_3$, $-OCOCH_3$ and NH_2 groups as substituents in the naphthalene ring was undertaken and the results are now reported in this paper.

Anthracene reacts with both sulphur monochloride and sulphur dichloride in presence of aluminium-mercury couple, to give anthracene-9 : 10-tetrathio dichloride, m.p. 257°. In the absence of a catalyst, however, anthracene and sulphur monochloride gave only anthracene-9-dithiochloride in confirmity with the experiments of Lippmann and Pollak (*Ber.*, 1901, 34, 2767) and contrary to those of Friedländer and Simon (*Ber.*, 1922, 58, 3969).
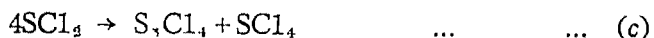
α-Naphthol reacts violently with sulphur dichloride but with sulphur monochloride it gives 4 : 4'-dihydroxydinaphthyl disulphide, m. p. 212° in small yields (*cf* Airan and Shah, *J. Univ. Bombay*, 1940, 9, *iii*, 120, 125 ; 1942, 10 *v*, 129). On treatment with sulphuryl chloride the latter produced 4-chloro-α-naphthol, m. p. 116-17° as an evidence of the structure assigned above. 2 : 2'-Dihydroxydinaphthyl sulphide was obtained with β-naphthol and sulphur chlorides, but with the monochloride, in addition, a trisulphide, m. p. 118° (substitution in 4 position) instead of the tetrasulphide as reported by Henrique (*Ber.*, 1894, 27, 2993) was obtained. The presence of hydroxyl groups in these compounds has been proved by acetylation and estimation of acetyl groups and the position of substitution of the sulphur residues, by bromination and also by treating with diazobenzene chloride. 2-Acetyl-α-naphthol gives with sulphur

dichloride, a monosulphide as well as a disulphide, the latter being produced when some alcohol is present in ether used for the reaction. In addition, a trisulphide could also be obtained (cf. Airan and Shah, loc. cit.).

1 : 2- and 2 : 3-Hydroxynaphthoic acids give only monosulphides but ∝- and β- acetoxynaphthalenes fail to react with the sulphur chlorides. ∝- and β- Naphthylamines react with sulphur monochloride and sulphur dichloride to yield two trisulphide hydrochlorides, m. p. 210^{0} and 115^{0} respectively. On treatment with sodium hydroxide, the free bases, m, p. 195^{0} and 150^{0}, unchanged by treatment with acetic anhydride, are obtained. Formulae (I) and (II) are provisionally assigned to these compounds (cf. Jacobson, Ber., 1887, 20, 1897 ; Hoffmann, ibid., p. 1798).

(I)   (II)
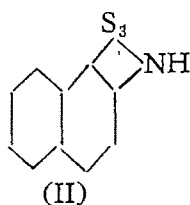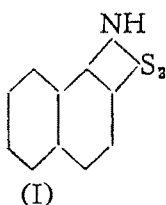
The formation of mono-, di- and trisulphides in the above reactions, can be easily explained on the basis of the following equations studied by various workers (Richter, Ber., 1917, 49, 1024 ; Marchand, Annalen, 1841, 40, 233) ; Lowry, McHatton and Jones, J. Chem. Soc., 1927, 746).

$$2S_2Cl_2 \rightarrow SCl_2 + S_3Cl_2 \qquad \ldots \qquad \ldots \quad (a)$$

$$2SCl_2 \rightarrow S_2Cl_2 + Cl_2 \qquad \ldots \qquad \ldots \quad (b)$$

$$4SCl_3 \rightarrow S_3Cl_4 + SCl_4 \qquad \ldots \qquad \ldots \quad (c)$$

The rapid inter-conversions of these compounds in situ appear to be responsible for the formation of the different types of the reaction products. It may also be pointed out in this connection that (i) the presence of catalysts like aluminium-mercury couple facilitates introduction of two -S_2Cl groups in anthracene ; (ii) hydroxy groups (cf. naphthols) activate the naphthalene nucleus with respect to the action of sulphur chlorides ; (iii) additional presence of CO_2H and $COCH_3$ groups has some modifying effect ; (iv) these reactions appear to proceed step by step as shown below.

$$R.S_2Cl \rightarrow R_2S_2 \rightarrow R_2S$$
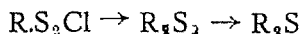
depending upon the activating influences of other groups ; and (v) the formation of trisulphides is readily accounted for, on the basis of the equation (a).

EXPERIMENTAL.

Naphthalene Dithiochloride.—To a solution of naphthalene (10 g.) in dry ether, sulphur monochloride (6 c. c.) was added, using bismuth chloride (0. 2 g.) as a catalyst. The reaction mixture was kept aside for a day.

On removal of the ether a plastic mass was obtained which was washed successively with hot methyl alcohol, hot ethyl alcohol, and finally with ether. Thus a granular compound was obtained which was then treated with carbon tetrachloride in a Soxhlet for further purification, m.p. 156°, yield 6.5 g. Sulphur dichloride gave identical product, but the yield was 1 g. only. (Found . Cl, 15.8 ; S, 28.4. $C_{10}H_7ClS_2$ requires Cl, 15.7 ; S, 28.3 per cent)

To 2 g. of the above compound, 15 c.c of concentrated nitric acid were added. The reaction was completed by warming. On cooling, the reaction mixture was poured over ice-water. A yellow compound separated, which melted at 58° (alcohol). Its mixed melting point with an authentic sample of ⍺-nitronaphthalene showed no depression.

Anthracene Dithiochloride.—To a suspension of anthracene (5 g.) in petroleum, sulphur monochloride (6 g.) was added. The reaction mixture was refluxed on a water-bath for a few minutes, when a reddish solution was formed. On cooling, a solid separated which was removed by filtration, and crystallised from benezene, m.p. 212°. (Found : Cl, 12.7 ; S, 23.3. $C_{14}H_9ClS_2$ requires Cl, 12.84.; S, 23.15 per cent).

Anthracene Tetrathiodichloride.—To a suspension of anthracene (10 g.) in dry ether, sulphur monochloride (10 c.c.) was added, using aluminium mercury couple as catalyst (*cf. J. Chem. Soc*, 1899, **75**, 887). The reaction mixture was kept overnight, and next day the ether was removed by distillation. The residue was washed with hot alcohol and hot benzene to remove the unacted anthracene. Finally the product was treated with carbon tetrachloride in a Soxhlet, m.p. 257°, yield 7.5 g. It was also obtained when sulphur dichloride was used instead of sulphur monochloride. (Found . Cl, 19.0 ; S, 34.4. $C_{14}H_xCl_2S_4$ requires Cl, 18.9 ; S, 34.1 per cent).

The above compound on oxidation with chromic acid in glacial acetic acid in the usual way gave anthraquinone.

4 : 4′-*Dihydroxydinaphthyl Disulphide.*—To a solution of ⍺-naphthol (10 g.) in dry ether, sulphur monochloride (5 g.) was gradually added when there was a visible reaction with a distinct change in colour of the reaction mixture. Next. day the reaction mixture was rapidly filtered, and ether was removed by distillation. The residual viscous mass was treated with glacial acetic acid, and filtered. The filtrate was diluted with water and left overnight. The solid mass now formed was taken up with the least quantity of ether, methyl alcohol added and scratched when a colourless solid separated out. It was filtered, and very rapidly washed with small quantities of methyl alcohol, yield 2 g. It was then crystallised from methyl alcohol, m. p. 212°. (Found : S, 18.3. $C_{20}H_{14}O_2S_2$ requires S, 18.28 per cent).

The *acetyl* derivative of the above compound was crystallised from alcohol, m.p. 172°. (Found : S, 7.8. C₂₁H₁₈O₄S requires, S, 7.9 per cent). This shows that during acetylation one sulphur atom is eliminated.

4 : 4'-Dihydroxydinaphthyl disulphide (4 g.) was taken in ether and treated with 2 c.c. of sulphuryl chloride. The excess of the reagent and the ether were removed by distillation. The residue was very rapidly washed with small quantities of ether, and then crystallised from alcohol, m.p. 116-17°. (Acetyl derivative, m.p. 44°). It was identical with 4-chloro-ⲁ-naphthol (*Ber.*, 1893, 26 3052), prepared by treating ⲁ-naphthol with sulphuryl chloride.

Reaction of Sulphur Monochloride with ⲁ-Naphthylamine.—ⲁ-Naphthyl-amine (5 g.) was dissolved in carbon tetrachloride and sulphur monochloride (3 c.c.) was gradually added with constant shaking. A dark chocolate solid immediately separated. The reaction mixture was refluxed on a water-bath for ½ hour, and then filtered, yield 8. 5 g. It is insoluble in water, alcohol, and chloroform. Advantage was taken of this to rid it of other compounds of sulphur sticking to it, by treating with carbon tetrachloride in a Soxhlet. This washing was repeated till a constant m. p. 210-12° (decomp.) was obtained. It did not appear to be a primary amine and was unaffected by boiling with water or hot concentrated hydrochloric acid. (Found : N, 4. 5 ; Cl, 13. 1 ; S, 35. 4. C₁₀H₈NClS₃ requires N, 5. 1 ; Cl, 13. 1 ; S, 35.1 per cent).

On being refluxed with a solution of sodium hydroxide a green solid was obtained, m.p. 200°. (Found ; N, 5. 9 ; S, 40.4. C₁₀H₇NS₃ requires N, 5. 9 ; S, 40. 3 per cent).

ⲁ-Naphthylamine and sulphur dichloride also gave the same product, m.p. 210-12°.

Reaction of Sulphur Monochloride with β-Naphthylamine.—β-Naphthyl-amine was treated with sulphur monochloride in the same way as described above. The compound was red in colour, and melted at 115°. It was repeatedly washed with benzene and carbon tetrachloride. When it was treated with cold water, a green solid was obtained which contained no chlorine. It was crystallised from alcohol in golden flakes or yellowish red needles, m.p. 150°, (decomp.). (Found : N, 6. 1 ; S, 40.5. C₁₀H₇NS₃ requires, N, 5. 9 ; S, 40.3 per cent).

β-Naphthylamine treated with sulphur dichloride in similar manner gave the same compound.

3 : 3'-*Diacetyl-4 : 4'-dihydroxydinaphthyl Disulphide.*—2-Acetyl-ⲁ-naphthol (10 g.) was dissolved in dry ether, and a small quantity of alcohol was added, using zinc chloride as a catalyst. Sulphur dichloride (5 c.c.) was then added and the reaction mixture kept aside A solid separated out,

which was filtered and crystallised from alcohol, m.p. 185°. Its mixed melting point with 3 : 3'-diacetyl-4 : 4'-dihydroxydinaphthyl sulphide (Airan and Shah, *loc. cit.*) was 170°. (Found : S, 14. 9. $C_{24}H_{18}O_4S_2$ requires S, 14. 7 per cent).

It gave an acetyl derivative identical with that of 3 : 3'-diacetyl-4 : 4'-dihydroxydinaphthyl sulphide.

2 : 2'-*Dihydroxydinaphthyl Trisulphide.*—When β-naphthol (10 g.) dissolved in dry ether was treated either with sulphur dichloride or with sulphur monochloride (5 g.), 2 : 2'-dihydroxydinaphthyl sulphide, m.p. 212° (Airan and Shah, *loc. cit.*) was obtained After the removal of this sulphide from the reaction mixture the ether was removed from the filtrate by distillation, the residue was dissolved in alcohol, and methyl alcohol was added when a yellow solid separated out. Purified by crystallisation from alcohol, it melted at 118°. (Found : S, 25. 1. $C_{20}H_{14}O_2S_3$ requires S, 25.01 per cent). It gave an acetyl derivative identical with that of 2 : 2'-dihydroxydinaphthyl sulphide.

The authors express their indebtedness to Dr. R. C. Shah of the Royal Institute of Science, Bombay, for his valuable suggestions and keen interest in this work.

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ACRIDINES AS ANTISEPTICS

By P. Das-Gupta and P. Gupta

Certain 5-(diethylamino-alkyl)-aminoacridines have been prepared. Their basicity as well as the antiseptic properties have been recorded.

Since the observations of Browning (*J. Path. & Bact.*, 1914, 18, 144), the salts of 2 : 8-diaminoacridines are being largely used as antiseptics. But they are often more toxic to leucocytes than to bacteria, become inactivated by absorption on cotton-dressings, and are found to cause sloughing in wounds on prolonged application. Recently, 2 : 7-diamino- and 5-amino-acridines have, however, been found to be somewhat free from the above drawbacks (*cf.* Albert *et. al., Quart. J. Pharm. & Pharmacol.*, 1937, 10, 649 ; Rubbo *et al., Brit. J. Path. & Bact.*, 1942, 23, 69).

Accordingly a systematic study on various 5-(diethylamino-alkyl)-aminoacridine derivatives is being made in this laboratory for the last few years (Basu and Bose, *Annal. Biochem & Exp. Med.*, 1941, 1, 317 ; Bose *et al., Ind. Med. Gaz.*, 1944, 79, 595, 601). These compounds are strong bases and as Albert has noticed that the bactericidal action of the acridine derivatives is associated with their basicity (*Nature*, 1941, 147, 332), an investigation was undertaken to study the bactericidal properties of various 5-(dialkylamino-alkyl)-aminoacridines prepared in this laboratory. In the meantime Lawrence and his collaborators (*J. Lab. Clin. Med.*, 1944, 29, 134, 1177) have noticed a strong bactericidal action in certain acridine derivatives of the above type. The investigations that have been so far carried out are being recorded in this paper.

Diethylamino-ethyl, -propyl, -β-hydroxypropyl, -butyl, -*iso*amyl amines have been condensed with 5-chloroacridine to afford 5-(diethylamino-ethyl), 5-(γ-diethylamino-propyl)-. 5-(γ-diethylamino-β-hydroxypropyl)-, 5(δ-diethylaminobutyl)-, and 5-(ω-diethylamino-*iso*amyl) aminoacridines. The basicity and the bactericidal properties of all these compounds have been studied. Besides, 2-chloro-7-methoxy-5-(δ-diethylamino butyl)-aminoacridine (*cf.* Basu and Bose, *loc. cit.*) was obtained by reacting the 5-chloroacridine derivative with δ-diethylamino-butylamine and tested for its basicity as well as bactericidal property. 2-Aminothiazole was also condensed with 5-chloroacridine, but the condensation product was found to possess no special bactericidal property.

FIG. 1
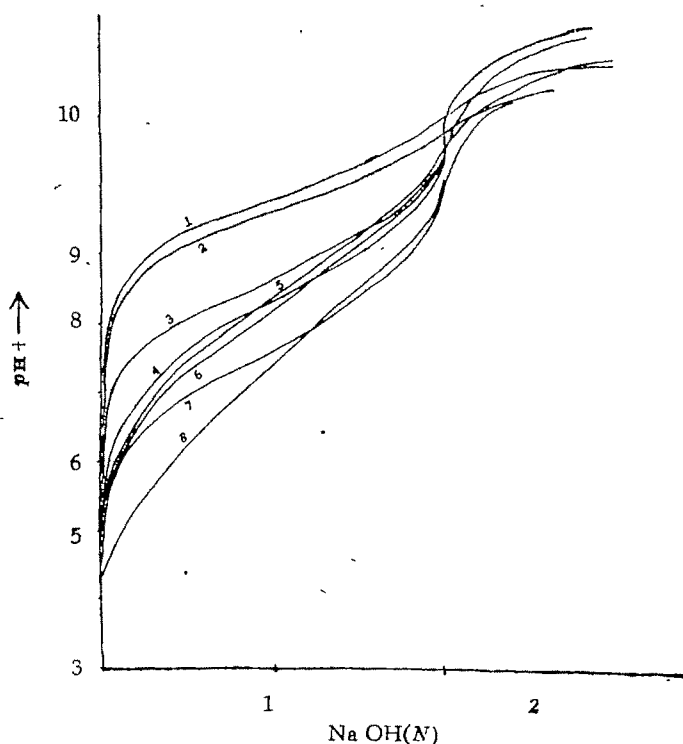
In the graph are shown the potentiometric titration curves of the dihydrochlorides of diethylamino-butyl- (3), -propyl-(5), -isoamyl-(4), -β-hydroxypropyl-(7), -ethyl-(3), - aminoacridines respectively and also of 2-chloro-7-methoxy-5-δ-diethylaminoacridine dihydrochloride (6) against alkali. The curves for proflavin (1) and 5-aminoacridine (2) (Albert, *loc. cit.*) are also included for comparison. Approximately 0.002 g. mole of crystalline hydrochloride in each case was dissolved in 25 c.c. of 50% ethanol and titrated against 0.5N-NaOH using hydrogen electrode in a titration cell having all-glass ground-in joints. The hydrogen used was electrolytically generated and carefully purified in the usual manner.

The acidity constants (pκa), calculated from the curves are shown i 1 Table I whence the basicity of the various derivatives would be easily noticed. It is evident that the 5-(diethylamino-alkyl)-aminoacridines are quite as basic as 5-aminoacridine. The antibacterial activity of this group of compounds would be evident from Table II.

Further work is in progress to study the influence of various nuclear substitutes on the basicity and consequently on the bactericidal property 5-aminoacridines.

TABLE I

No	Compound.	Solubility of the di-hydrochloride in 95% ethanol at 33° (room temp.)	pH of the dihydrochloride in water		pKa
			1% soln.	2% soln.	
1	Proflavine	—	—	—	9.5 (Albert)
2	5-Aminoacridine	—	—	—	9.34 (Albert)
8	5-(Diethylaminoethyl-amino)-acridine	1 in 30	5.3	5 1	7.35
5	5-(Diethylaminopropyl-amino)-acridine	1 in 11	5.8	5,5	8.6
3	5-(Diethylaminobutyl-amino)-acridine	1 in 11	5.8	5.5	8 6
4	5-(ω-Diethylamino-iso-amylamino)-acridine	1 in 14	6 1	5.8	8.3
7	5-(γ-Diethylamino-β-hydroxypropylamino) acridine	1 in 100	5 4	5.3	7.6
6	2-Chloro-7-methoxy-5-(δ-diethylaminobutyl amino)-acridine	1 in 150	4.9	4.5	8.2

TABLE II

Bacteriostatic property

Minimal inhibiting concentration in mg. of the compound
per 100 c.c. of culture media

Serial Number.	Compound.	Staphylo aureus.	Streptococcal (Haemo).	B Coli.	Proteus.	Pyocyaneus
1.	Acriflavine	1	0.2	2	10	20
2.	5-Aminoacridine	2	1	2	2	10
4.	isoAmyl ,,	10	0 5	20	50	100
3.	Butyl ,,	2	0.2	4	10	20
5.	Propyl ,,	2	0.2	2	4	10
7.	Hydroxy-propyl	4	1	4	20	50
8.	Ethyl ,,	10	2	10	50	100
6.	Compound 6	1	0.2	4	50	50

EXPERIMENTAL

5-(*Diethylaminoethyl*)-*aminoacridine* *Hydrochloride.*—5-Chloroacridine (2 g.) was dissolved in phenol (10 c.c) at 100-110° and diethylamino-ethylamine (1 g.) was dropped into it with stirring during the course of ¼ hour, and the mixture heated at the same temperature for about 2 hours more. It was cooled and diluted with benzene. The mixture was made alkaline with sodium hydroxide and shaken in a separating funnel. The benzene solution obtained was treated with dilute acetic acid and the

whole thing extracted repeatedly with water. The aqueous solution was basified with dilute ammonia and extracted with ether. The ethereal solution was dried with potassium carbonate and dry hydrogen chloride passed through it whereby the dihydrochloride of 5-(diethylaminoethyl)-aminoacridine was obtained as yellow crystals. The solid isolated was recrystallised from a mixture of acetone and alcohol, m.p. 249-50°. (Found : N, 11.3 ; Cl, 18.7 ; H_2O, 4.3. $C_{19}H_{23}N_3$, $2HCl_0$ H_2O requires N, 10.9 ; Cl, 18.5 ; H_2O, 4.68 per cent). The dihydrochloride is highly soluble in water, and an 1% solution of it is not salted out of normal saline. On keeping with sodium citrate solution, however, a crystalline precipitate, m.p. 350°, separates out. The base liberated by adding dilute ammonia to the hydrochloride solution is a viscous semi-solid mass forming a picrate, m. p, 205°. [Found : N, 17.0. $C_{19}H_{23}N_3,2C_6H_2(OH)(NO_2)_3$ requires N, 16.8 per cent]. Auric chloride compound, m. p. 120° (indifferently). (Found : Au, 41.0.C$_{19}H_{23}N_3$. $2HAuCl_4$ requires Au, 40.5 per cent].

5-(γ-Diethylaminopropyl)-aminoacridine Hydrochloride.

—Diethylaminopropylamine (1.3 g.) was reacted with 5-chloroacridine (2.1 g.) in a manner similar to the previous case and the dihydrochloride of 5-(γ-diethylaminopropyl)-aminoacridine isolated in a similar manner. The final product is a yellow crystalline solid, m.p. 230° when crystallised from a mixture of acetone and alcohol, yield 3 g. (Found : N, 10. 63 ; Cl, 17.76 ; H_2O, 4.52, $C_{20}H_{25}N_3$, $2HCl$, H_2O requires N, 10.5 ; Cl, 17.83 ; H_2O, 4.5 per cent).

The dihydrochloride is very soluble in water. The base is a viscous semi-solid mass forming a picrate, m. p. 197°. [Found : N, 16.6. $C_{20}H_{25}N_3$, $2C_6H_2(OH)(NO_2)_3$ requires N. 16.47 per cent].

5-(δ-Diethylaminobutyl)-aminoacridine Hydrochloride.

—5-Chloroacridine (2.1 g.) and δ-diethylaminobutylamine (1.4 g.) were reacted together in a manner similar to the previous cases and 5-(δ-diethylaminobutyl)-aminoacridine dihydrochloride isolated as above. The yellow crystals were very soluble in water and melted at 237-38°. (Found : N, 10.36 ; Cl, 16.7 ; H_2O, 4.5. $C_{21}H_{27}N_3,2HCl$, H_2O requires N, 10.2 ; Cl, 17.2 ; H_2O, 4.4 per cent).

The base, liberated by adding ammonia to the hydrochloride solution is a semi-solid viscous mass forming picrate, m. p. 203-204°. [Found : N, 16.3. $C_{21}H_{27}N_3$, $2C_6H_2(OH)(NO_2)_3$ requires N, 16.1 per cent).

The chloroplatinate melts at 200-210° (decomp.). (Found : Pt, 26.5. $C_{21}H_{27}N_3$, H_2 $PtCl_6$ requires Pt, 26.7 per cent).

5-(ω-Diethylaminoisoamyl)-aminoacridine - Hydrochloride.

—5-Chloroacridine (2.1 g,) was reacted as usual with ω-diethylaminoisoamylamine (1.6 g.) in phenol medium and the dihydrochloride of 5-(ω-diethylaminoisoamyl)-aminoacridine isolated as above, m. p. 194°, yield

3 g. It is very soluble in water. (Found: N, 10.19; Cl, 16.5; H$_2$O, 3.83. C$_{22}$H$_{29}$N$_1$, 2HCl, H$_3$O requires N, 9.85; Cl, 16.6 H$_2$O, 4.2 per cent). The base was obtained as a semi-solid viscous mass which forms a pictate, m. p. 170°. [Found: N, 16.1. C$_{22}$H$_{19}$N$_3$, 2C$_6$H$_2$ (OH) (NO$_2$)$_3$ requires N, 15.9 per cent].

5-(γ-Diethylamino-β-hydroxypropyl)-aminoacridine   Hydrochloride.— 5-Chloroacridine (2.1 /g.) was reacted with γ-diethylamino-β-hydroxy propylamine (1.5 g.) as above and the dihydrochloride of (γ-diethyl-amino-β-hydroxypropyl)-aminoacridine isolated as usual.

It is a yellow crystalline solid, highly soluble in water and melts at 230°. (Found: N, 10.6; Cl, 17.0; H$_2$O, 2.3 C$_{20}$H$_{15}$O$_2$N$_3$ 2HCl, ½H$_2$O requires N, 10.4; Cl, 17.5; H$_2$O, 2.2 per cent).

The base liberated from the hydrochloride solution by dilute ammonia is a solid, m. p. 88-89°.

*5-(2'-Aminothiazol)acridine.—*5-Chloroacridine (2.1 g.) was taken in 10 c. c. anhydrous phenol and 1. g. of 2-aminothiazole added to it gradually during the course of half an hour, the temperature being maintained at 100-110°. The reaction mixture was heated for 2 hours more. The cold mass was basified with dilute sodium hydroxide in cold and taken in benzene. The benzene solution was treated with dilute acetic acid and the acetic acid solution obtained basified with ammonia whereby the base 5-(2-aminothiazolyl)acridine was obtained as a solid. This was crystallised from dilute alcohol in slender needles, m. p. 235°. (Found: N, 14.9; S, 13.1, C$_{16}$H$_{11}$N$_3$S requires N, 15.15; S, 13.3 per cent).

The base forms a hydrochloride which can be crystallised from dilute alcohol in beautiful needle-shaped crimson-coloured crystals. m. p. 250°. It is sparingly soluble in water.

REVIEWS

The Measurement of Colour BY W. D. WRIGHT. PUBLISHED BY ADAM HILGER LTD. LONDON, 1944. Pp, viii + 224. PRICE 30s. NET.

This book gives an account of the principles, methods and applications of the trichromatic system of colour measurement. As mentioned in the preface of the book, only methods based on the trichromatic system formulated in 1931 by the Commission Internationale de l'E'Clairge have been discussed.

The first chapter deals with some properties of light in the visible region, such as spectral distribution of energy, adsorption, reflection etc. Chapter II gives a brief description of the eye and its relative sensitivities to light of different colours. The definitions of some fundamental units for measurement of light are also found in this chapter.

The development of the trichromatic system, derivation of the unit trichromatic equation, representation of colour in two dimensional diagram, the locus of visible spectrum in the chromaticity diagram etc. have been dealt with in Chapter III, The main features of colorimeters have been described in Chapter IV and Chapter V contains a brief description of a few spectrophotometers and discussions regarding their uses in colour measurement.

Chapter VI deals with the colour at least as a sub-standard of colour measurement and the famous Munsell system for the representation of colours in three dimensional co-ordinate system has also been explained in this chapter with the help of suitable diagrams.

The last chapter contains a very useful discussion about the application of colorimetry in agriculture, meteorology and in several industries, viz., lighting, chemical and clinical, pulp and paper, paint, signal glasses, colour reproduction industry etc.

There are three valuable appendices, the first describing the four standard illuminants, the second containing tables of values of trichromatic and other coefficients required for measurement of colour and the third contains condensed tables of values of distribution coefficients etc. useful for colour computation.

As the subject of measurement of colour has been developed only recently and the terminologies and conventions adopted from time to time are quite complicated, this book dealing lucidly with the principles of the methods and technique employed will be of immense use to those who want to use a colorimeter either in any industry or in any other scientific investigation.

The book is amply illustrated, there being altogether sixty five diagrams of which six are multi-coloured. Probably it is the consideration of the high cost of these coloured blocks which led the publishers to fix the price of this book at 30s. net. This price, however, seems to be a little too high.

S. C. S.

Recent Advances in the Chemistry and Biology of Sea-water BY H. W. HARVEY, Sc. D., F. R. S., CAMBRIDGE UNIVERSITY PRESS, 1945. Pp 164. PRICE 10s. 6d. NET.

The book consists of ten chapters dealing with the physical, chemical and biological aspects of sea water. The major constituents of sea water are as follows.—$Na^{\cdot}$ 30.4%, $Mg^{\cdot\cdot}$, 3.7%, $Ca^{\cdot\cdot}$, 1.16%, $K^{\cdot}$, 1.1%, $Sr^{\cdot\cdot}$, 0.04%, Cl', 55.2%, SO_4'', 7.7%, Br'', 0.19%, H_3BO_3, 0.07%, HCO_3' & CO_3'', 0.35%.

The minor constituents consisting of at least 45 elements including uranium, vanadium, gallium, cerium, scandium, lanthanum, yttrium, radium, mercury, silver, gold, etc. form only 0.025% of the major constituents. It is interesting to note that Professor Haber, who carried on important experiments for the extraction of gold from sea water with the chief object of repaying the indemnity demanded by the allies in world war I after the defeat of Germany estimated in 1928 that sea water contains 0.004 mg. of gold per cubic metre of sea-water, whilst the recent work of Prof. Noddack (1940) shows that the amount of gold may be 0.008 milligram per m^3. The author has collected the results regarding the amount of oxygen, nitrogen and carbon dioxide dissolved in sea water at different depths. The distribution and estimation of phosphate, ammonium salts, nitrite and nitrate have also been carefully considered and the possibility of the photoformation of nitrite and nitrate by the oxidation of ammonium salts has been discussed. The micro-organic population and its influence on the decomposition of organic matter and of dead plankton organisms and the fertility of ocean waters have been carefully considered. The book contains an author index and a subject index and is an useful publication dealing with a large ammount of researches in which the author has taken an important part on the relation of plant and animal life and the major and minor chemical constituents of ocean water.

N. R. D.

Manufacture of Lead and Slate Pencils BY PROFESSOR N. N. GODBOLE, BENARES HINDU UNIVERSITY.

This small booklet contains 40 pages and eight chapters. All the contents of the booklet were written 28 years before as has been indicated by the author in his foreward. Of the eight chapters the one on selection

of wood (Chapter III) has been ably written and chapter on the methods of manufacture may be valuable to those interested in cottage industries. The antidated articles (1917) without any reference and consideration of the present position of the industries intertwined with insufficient and inaccurate statistics are realy drawbacks which will perhaps be removed by a future publication not hasty like the present one. From a technological point of view, chapters on standardisation of proper wood together with processes of softening, or graphite, clay and glue used and description of machines with drawings and brief engineering details should have been included.
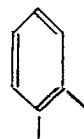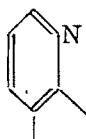
M. N. G.

ERRATA

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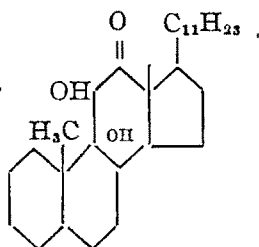
19   Structure II

19-20   The word " *dihydroxy artostenone* " should be read as " dihydroxy artostanone " throughout the paper.

219   Structure II

258   33   3-Amino-4-hydroxyphenylarsonic acid   3-Amino-2-hydroxyphenylarsonic acid

285   10   *Add* after solution " should readily dive under light touch some solution "

261   End of 3rd paragraph   *Z. physikal. Chem.*, 1929, **4**B, 299   *Z. physikal. Chem.*, 1929, **4**8, 299.

Facing 264   Fig. 1, the arrow should be shifted left coinciding the first line in that group of lines.

Page	Line	Read	for
269	6	author	authot.
,,	7	(. . . 1940, 1**4**, . . .)	(. . . 1929, 1**4**, . . .).
,,	10	acetone	atetone.
290	Table I, column 4	$NH_4H[O(MoO_3)_{4\cdot4}]$	$NH_4H[O(MoO_3)_{4\cdot9}]$.
293	,, IVA, ,, 1	$Na_2[OMoO_3)_8]$	$Na_2[O(MoO_{38})]$.
,,	,, IVB, ,, 1	$Na_2[O(MoO_3)_8]$	$Na_2[O(MoO_3)_8$.